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16. ABSTRACT

This guideline document has been prepared to augment the information previously released by the Office of Federal Activities entitled Environmental Impact Assessment Guidelines for Selected New Source Industries. Its purpose is to provide guidance for the preparation and/or review of environmental documents (Environmental Information Document or Environmental Impact Statement) which EPA may require under the authority of the National Environmental Policy Act (NEPA) as part of the new source (NPDES) permit application review process.

This document has been prepared in seven sections, organized in a manner to facilitate analysis of the various facets of the environmental review process. The initial section includes a broad overview of the industry intended to familiarize the audience with the processes, trends, impacts and applicable pollution regulations commonly encountered in the phosphate fertilizer industry. Succeeding sections provide a comprehensive identification and analysis of potential environmental impacts, pollution control technologies available to meet Federal standards, and other controlable impacts. The document concludes with three sections: available alternatives, a listing of Federal regulations (other than pollution control) which may apply to the new source applicant, and a comprehensive listing of references for further reading.

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ENVIRONMENTAL IMPACT GUIDELINES FOR NEW SOURCE PHOSPHATE FERTILIZER MANUFACTURING FACILITIES

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US Environmental Protection Agency
Office of Federal Activities
Washington, D.C. 20460

Preface

This document is one of a series of industry-specific Environmental Impact Guidelines being developed by the Office of Federal Activities (OFA) for use in EPA's Environmental Impact Statement preparation program for new source NPDES permits. It is to be used in conjunction with Environmental Impact Assessment Guidelines for Selected New Source Industries, an OFA publication that includes a description of impacts common to most industrial sources.

The requirement for Federal agencies to assess the environmental impacts of their proposed actions is included in Section 102 of the National Environmental Policy Act of 1969 (NEPA), as amended. The stipulation that EPA's issuance of a new source NPDES permit as an action subject to NEPA is in Section 511(c)(1) of the Clean Water Act of 1977. EPA's regulations for preparation of Environmental Impact Statements are in Part 6 of Title 40 of the Code of Federal Regulations; new source requirements are in Subpart F of that Part.

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INTRODUCTION

The Clean Water Act requires that the United States Environmental Protection Agency (USEPA) establish standards of performance for categories of new source industrial wastewater dischargers. Before the discharge of any pollutant to the navigable waters of the United States from a new source in an industrial category for which performance standards have been proposed, a new source National Pollutant Discharge Elimination System (NPDES) permit must be obtained from either USEPA or the State (whichever is the administering authority for the State in which the discharge is proposed). The Clean Water Act also requires that the issuance of a permit by USEPA for a new source discharge be subject to the National Environmental Policy Act (NEPA), which may require preparation of an Environmental Impact Statement (EIS) on the new source. The procedure established by USEPA regulations (40 CFR 6 Subpart F) for applying NEPA to the issuance of new source NPDES permits may first require preparation of an Environmental Information Document (EID) by the permit applicant. Each EID is submitted to USEPA and reviewed to determine whether there are potentially significant effects on the quality of the human environment resulting from construction and operation of the new source. If there are, USEPA publishes an EIS on the action of issuing the permit.

The purpose of these Guidelines is to provide industry-specific guidance to USEPA personnel responsible for determining the scope and content of EID's and for reviewing them after submission to USEPA. It is to serve as supplementary information to the previously published Environmental Impact Assessment Guidelines for Selected New Source Industries (USEPA 1975), which includes the general format for an EIA and those impact assessment considerations common to all or most industries. Both that document and these Guidelines should be used in the development of an EID for a new source phosphate fertilizer manufacturing facility.

These Guidelines provide the reader with an indication of the nature of the potential impacts on the environment and the surrounding region from construction and operation of phosphate fertilizer plants. In this capacity, the volume is intended to assist USEPA personnel in the identification of those impact areas that should be addressed in an EID. In addition, these Guidelines present (in Section 1.0) a description of the industry; demand for industry output, its principal processes and environmental problems; and recent trends in location, raw materials, processes, pollution control, and environmental impacts. This "Overview of the Industry" is included to familiarize USEPA staff with existing conditions in the industry.

Although this document may be transmitted to an applicant for informational purposes, it should not be construed as representing the procedural requirements for obtaining an NPDES permit or as representing the applicant's total responsibilities relating to the new source EIS program. In addition, the content of an EID for a specific new source application is determined by USEPA in accordance with Section 6.604(b) Title 40 of the Code of Federal Regulations and this document does not supersede any directive received by the applicant from USEPA's official responsible for implementing that regulation.

These Guidelines are divided into six sections. Section 1.0 is the "Overview of the Industry," described above. Section 2.0, "Impact Identification," discusses process-related wastes and the impacts that may occur during construction and operation of the facility. Section 3.0, "Pollution Control," summarizes the technology for controlling environmental impacts. Section 4.0 discusses other impacts that can be mitigated through design considerations and proper site and facility planning. Section 5.0, "Evaluation of Alternatives," summarizes possible alternatives to the proposed action and discusses evaluation of their consideration and impact assessment. Section 6.0 describes regulations other than pollution control that apply to the industry. Section 7.0 is a list of references, arranged by topic, which are useful for additional or more detailed information.

1.0 OVERVIEW OF THE INDUSTRY

These Guidelines deal with phosphate fertilizer manufacturing in the United States as it is today and as it is presently evolving. "Phosphate Fertilizer Manufacturing" refers to that industry which takes phosphate rock, a relatively insoluble raw material, and processes it to produce a number of water-soluble phosphorus-containing chemicals which are further utilized in the manufacture of fertilizers. The products of these processes are fertilizer materials, some of which could be applied directly. In practice this is rarely done because most areas which can benefit from fertilizers suffer from soil deficiencies besides that of available phosphorus. For most purposes, then, the phosphate fertilizer industry produces intermediate products which are used in other segments of the fertilizer or inorganic chemical industries.

Some phosphate fertilizer plants produce a single product primarily, while others are integrated complexes which produce a full range of phosphate fertilizer products, and may produce a number of other chemical products at the same facility. It is common for one company to be involved in industry segments ancillary to phosphate fertilizer manufacture. For example, many companies are located at or near the mine site for phosphate rock and may be involved both in the ore extraction and processing as well as in the manufacturing processes to produce phosphate fertilizers or other phosphate chemicals.

The inter-relationships and distinctions among industry segments can be summarized as follows:

1) Phosphate mining industry - this is a segment of the mining industry which extracts phosphate ores and processes them to produce marketable quality "phosphate rock". Most ores are sedimentary deposits of the mineral fluorapatite and associated impurities, along with clays, sands, or other rock matrix. These constituents usually must be separated to concentrate the phosphate bearing deposits which are referred to as "phosphate rock," "phosrock", "phosphate rock concentrate", and "beneficiated phosphate rock." The phosphate mining industry is described more fully in Section 1.3.1.

2) Phosphate fertilizer industry - as described before, this industry uses phosphate rock from the phosphate mining processes and manufactures phosphate fertilizer chemicals.

3) Non-phosphate fertilizer industries - in reference to the phosphate fertilizer industry, these industries include the "nitrogen" or "nitrogenous" fertilizer industry and the "potassium" or "potash" fertilizer industry. A minor, often overlooked, industry engaged in fertilizer production is the "natural" or "organic" fertilizer industry. The products of the nitrogen and potash fertilizer industries are also usually considered intermediate products, which are combined with other materials or processed further for specific applications.

4) Mixed (and blended) fertilizer industry - this is the industry which actually produces most of the fertilizer materials commercially marketed. Phosphate, nitrogen, and potassium fertilizer chemicals, along with various fillers, coating agents, insecticides, and other useful additives are combined by this industry to produce popular blends or formulations tailored to the needs of certain geographic areas. In the parlance of the industry, "mixed fertilizer" refers to a fertilizer containing more than one of the primary plant nutrients (phosphorus, nitrogen, potash). There are three types of mixing plants:

- Bulk blending plants physically mix dry fertilizer materials, without chemical reaction, to produce a dry, granular mixed fertilizer.
- Ammoniation-granulation plants chemically react liquid and/or dry raw materials in a granulator to produce a dry fertilizer with the constituent nutrients blended in each granule.
- Liquid mixing plants are either "hot" or "cold". Hot mix plants are termed "hot" because of the exothermic reaction between phos-

phoric acid and ammonia; they produce a liquid mixed fertilizer. Cold mix plants physically mix liquid materials to derive a liquid mixed fertilizer without a chemical reaction (USEPA 1976f).

Rapid developments are underway in the mixed fertilizer industry. New liquid fertilizers are being developed and promoted with concurrent development of improved spreading equipment. Slurry-type mixtures are being marketed as fluid fertilizers, to be applied using conventional liquid spreading machinery.

5) Phosphorus and non-fertilizer phosphate industries - USEPA effluent guidelines and standards have established the "non-fertilizer" terminology to encompass the manufacture of certain phosphorus-derived chemicals that are widely used for purposes other than soil fertilization. This broad industry category includes the production of phosphorus and ferrophosphorus by smelting phosphate ore; production of phosphoric acid, phosphorus pentoxide, phosphorus trichloride, and phosphorus oxychloride directly from elemental phosphorus; production of sodium tripolyphosphate and animal feed grade and human food grade calcium phosphate from phosphoric acid; defluorination of phosphate rock by high temperature and other treatments; defluorination of phosphoric acid; and purification of sodium phosphates from wet process phosphoric acid (the "wet process" is described in detail in Section 1.3.2.4). The above processes produce products used in such applications as human food additives and animal feed supplements, plastics manufacture, metal treating, detergent builders, and incendiary chemicals.

For the most part, the industry segments other than the phosphate fertilizer industry will not be discussed further in these Guidelines. They will, however, be referred to, due to the interrelationships of industry segments.

Mixed fertilizers are usually described based on their NPK formulation - that is, on the ratio by weight of the percentage of nitrogen, phosphorous, and potassium contained in the formulation. For example, the formulation for a typical mixed liquid fertilizer (ammonium polyphosphate) is 11-37-0, meaning that 11% of the weight is nitrogen, 37% is phosphorus (expressed as P_2O_5 equivalent), and none is potassium. These ratios are also referred to as "nominal grades" based on their identification of the percentages of each primary nutrient irrespective of the type of chemical compound in which each may occur.

The NPK formulation is not a descriptor normally used for the basic phosphate fertilizer chemicals with the exception of ammonium phosphates. Because of their economic importance as an intermediate to numerous bulk blended and liquid fertilizers and because the production processes for ammonium phosphates are commonly performed in phosphate fertilizer complexes, effluents from these processes are frequently combined with the waste streams from other phosphate fertilizer processes and treated together. For these reasons, ammonium phosphates are covered under phosphate fertilizer industry effluent and emissions guidelines rather than those for mixed fertilizer industries, and are included in this Guidelines document.

For phosphate rock and its products the phosphorus content is commonly expressed in one of four ways:

- BPL (bone phosphate of lime or tricalcium phosphate - $Ca_3(PO_4)_2$)
- Phosphorus pentoxide (P_2O_5)
- Elemental phosphorus (P_4)
- Phosphoric acid (H_3PO_4)

The common industry practice is to report all phosphorus-containing materials in terms of the equivalent content of phosphorus pentoxide (P_2O_5). That practice is used throughout this document, unless otherwise stated.

The table below illustrates the relationships among the four sets of units:

Conversion factors for phosphorus content units.

To convert from	To	Multiply by
% H_3PO_4	% P	0.316
% H_3PO_4	% P_2O_5	0.724
% BPL	% P	0.1997
% BPL	% P_2O_5	0.4576
% P_2O_5	% H_3PO_4	1.381
% P_2O_5	% BPL	2.1853

Source: U.S. Environmental Protection Agency. 1979a. Source assessment: Phosphate fertilizer industry. Office of Research and Development, Washington, D.C. Prepared by Nyers, J.M., G.D. Rawlings, E.A. Mullen, C.M. Moscowitz, and R.B. Reznik, Monsanto Corp., Dayton OH, 201 p.

For example, orthophosphoric acid (phosphoric acid concentrated to its highest common H_3PO_4 content) would be expressed as 75% H_3PO_4, 54% P_2O_5, and 24% P.

1.1 SUBCATEGORIZATION

Effluent Guidelines and Standards (commonly called "effluent guidelines") are established by USEPA for specified pollutants which are regulated at specified allowable levels for various industry segments (Point Source Categories). In the Code of Federal Regulations USEPA sets forth effluent guidelines under Part 418 for the Fertilizer Manufacturing Point Source Category (40 CFR 418). This Guidelines document applies only to Subpart A, Phosphate Subcategory, of 40 CFR 418.

The provisions of the Phosphate Subcategory apply to discharges resulting from the manufacture of:

- sulfuric acid by sulfur burning;
- wet process phosphoric acid;
- normal superphosphate;
- triple superphosphate; and
- ammonium phosphates.

The five regulated processes represent those processes which, due to either the character or the quantity of their wastes, produce effluent streams capable of significant environmental degradation, as identified in the Development Document for the Fertilizer Manufacturing Point Source Category (USEPA 1974a). There are four additional processes (described in Section 1.3) for which either no waste stream is normally produced or the waste stream is regulated under one of the other processes with which it is closely associated. The nine basic processes can be described as follows:

- Sulfuric Acid by Sulfur Burning is the dominant process in the United States. Virtually all plants use sulfuric acid to treat the raw phosphate rock (acidulation) and produce phosphoric acid. Sulfuric acid is usually produced on the premises by burning molten sulfur in the presence of air to produce SO_2 gas. In the usual process, known as the "contact process," the SO_2 is further oxidized to form SO_3 using a catalyst contact surface. The sulfur trioxide (SO_3) gas is then hydrolized in a number of steps by the addition of water to form sulfuric acid (H_2SO_4) of the required concentrations.

- Phosphate Rock Processing - Crushing, Grinding, and Screening reduces the phosphate rock feedstocks to sizes optimal for reaction in further processes. This operation may be performed at a processing plant associated with the mine, at a central point in a fertilizer plant, or as a beginning operation feeding into another process.

- Normal Superphosphate Production is a process which was initially developed more than a century ago. Ground phosphate rock is reacted with sulfuric acid to produce a water-soluble but, by today's standards, low analysis phosphate.

- Wet Process Phosphoric Acid Production is the foundation of the phosphate fertilizer industry. Ground phosphate rock and sulfuric acid are reacted to form phosphoric acid and to precipitate calcium, sulfur, and other unwanted materials in insoluble forms that can be separated from the acid. The product, when completely processed, is an intermediate used to produce high analysis fertilizers.

- Phosphoric Acid Concentration is a continuation of the processing of wet process phosphoric acid whereby water is removed to improve concentration and reactability of the acid and also to improve shipping and storing efficiencies when sold as a product.

- Phosphoric Acid Clarification completes the processing of wet process phosphoric acid. Solids are caused to floculate or precipitate and are separated to avoid later problems in storage and handling. If not removed early in the production of the acid, solids will precipitate out as the acid ages in forms and locations that can incapacitate handling and process equipment.

- Superphosphoric Acid Production is a process to remove additional water and further concentrate the P_2O_5 equivalent content of phosphoric acid. The product is used in production of certain high analysis fertilizers.

- Triple Superphosphate Production reacts phosphoric acid with phosphate rock to produce a high analysis solid fertilizer which can be applied directly or can be used as a feedstock in the preparation of high analysis mixed fertilizers.

- Ammonium Phosphate Production yields highly concentrated sources of water soluble plant food which combine nitrogen and phosphorus in a single granule. The product is less bulky than dry mixes of N and P straight fertilizers, and easy to apply and handle due to the granular form in which it is usually produced. The granular form mitigates caking and dust problems. In addition, ammonium phosphates are more profitable to produce than some other products such as triple superphosphates.

As a chemical category, ammonium phosphates include monoammonium phosphate (MAP), diammonium phosphate (DAP), and a vast range of other ammoniated phosphates containing different ratios of ortho- and polyphosphate molecular components called collectively ammonium polyphosphates (APP). MAP and DAP are the "ammonium phosphates" included in the regulated processes of the Phosphate Subcategory (40 CFR 418). APP's are regulated under Subpart G, Mixed and Blend Fertilizer Production Subcategory. The essential distinction is that MAP and DAP are included in the Basic Fertilizers Phosphate Subcategory because they are produced at the same plants as the other basic phosphate fertilizer materials, even though they are technically mixed, containing both N and P nutrients. APP's on the other hand are produced in the numerous mixing plants in areas of application throughout the country. APP's are produced by reacting superphosphoric acid and ammonia or, in recent process improvements, phosphoric acid and ammonia, which are basic or straight fertilizer materials shipped into the mixing plants from basic fertilizer manufacturers.

1.2 MARKETS AND DEMANDS

The markets and economics of fertilizer use indicate a worldwide trend toward increasing overall demand on which are superimposed sometimes widely fluctuating market conditions from year to year. Demand is expected to continue increasing, but a host of variables confound the best efforts of industry experts accurately to predict short-term specific product demands. Despite these uncertainties, and allowing for reluctance by industry spokesmen to announce expansion plans before commitments are firm and site properties secured, the phosphate fertilizer industry appears to be increasing long-range production capacities.

United States demand for phosphates has grown steadily since World War II with rapid growth since 1965. Growth has been based on the farmer's need to maximize yield, but the market has been stimulated by the development of new fertilizer products which make application easier and less costly. Mixed fertilizers account for 85.18% of current phosphate fertilizer consumption (TVA 1979). These products incorporate a balance of NPK nutrients in a dry blend or liquid mix, and also can include sulfate, micronutrients, lime, soil conditioners, and pesticides. Thus, with timed release coatings, fertilization and pest control that used to require several operations, can be done at one time. In addition, local plants market soil analysis services as part of their product. Fertilizers are blended in these plants to supply the needs of the particular soil, and the company delivers and may even apply the fertilizer mix.

Production and consumption patterns of phosphate rock products are decidely toward a continuing concentration in wet process phosphoric acid production, which reflects the market for concentrated P_2O_5 content and mixed and blend final fertilizer products. Rock consumption in normal superphosphate (NSP) declined sharply in 1978. NSP is a product of low P_2O_5 content and diminishing importance, which is now manufactured primarily in small, low technology plants in close proximity to the sales area. NSP is used primarily as a direct application fertilizer or as a constituent in some dry blended fertilizers. Production of triple superphosphate has remained at a level of 5% to 6% of total phosphate fertilizer production, for use in dry blended fertilizers primarily. The most recent production figures for phosphate rock and P_2O_5 content are broken down by product use in Table 1.

Largely through the efforts of the United Nations Food and Agriculture Organization (FAO), the United States Agency for International Development (AID), the Tennessee Valley Authority (TVA), and other United States institutions and businesses, overseas interest in fertilizer use has grown into a substantial market. The effectiveness of fertilizers has been a foundation for many achievements of the "green revolution" in agriculture. That plus the huge United States market and limited long-term United States supplies, have brought new foreign competitors into the phosphate fertilizer field. Among them, Morocco stands alone as the potential "Saudi Arabia" of phosphate rock. With proven reserves of at least 10 billion tons of phosphate rock, Morocco holds 62.2% of the 16.065 billion-ton world reserve, which is based on economically recoverable rock at 1974 prices. The United States holds a reserve of roughly 2.5 billion tons. Furthermore, the Moroccan reserve may be as large as 40 billion tons (Stowasser 1975). From 1964 to 1973, the United States exported approximately 23% of domestic production (Stowasser 1977) and accounted for roughly 38% of world production (USEPA 1978b). The USSR and Morocco accounted for approximately 20% and 17%, respectively, of world production, and both countries are currently increasing production capacity. More recently, figures for United States phosphate exports, excluding phosphate rock, show increases in United States exports (Harre in TVA 1978a) (Table 2 and Figure 1).

Despite recent improvements in the United States export market, producers are accustomed to unprofitable periods of one or more years as large fluctuations have traditionally occurred in both exports and domestic consumption. The markets are extremely sensitive to price, as was indicated in 1975 when inventory buildup of phosphate rock abruptly exceeded demand after five years of short supply (TVA 1977a). This sudden lack of sales was due to higher prices set by the industry to offset costs of recent capital expansion. In that instance, Morocco cut prices drastically to stimulate sales, and United States suppliers were forced to follow suit. The most recent summary of production and dollar values of U.S. phosphate rock is given in Table 3.

Table 1. Phosphate rock sold or used by producers in the United States for all uses (1000 metric tons).

Use	1977 Rock	1977 P_2O_5 Content	1978 Rock	1978 P_2O_5 Content
Domestic:				
Wet process phosphoric acid	27,024	8,377	29,322	9,000
Normal superphosphate	913	283	298	93
Triple superphosphate	1,852	587	1,781	571
Defluorinated rock	298	99	193	65
Direct applications	36	7	39	7
Elemental phosphorus	3,904	1,011	4,371	1,135
Ferrophosphorus	180	46	200	52
Total (1)	34,207	10,410	36,204	10,923
Exports	13,230	4,251	12,570	4,025
Grand Total (1)	47,437	14,660	48,774	14,948

(1) Data may not add to totals shown because of independent rounding.

Source: U.S. Department of the Interior, Bureau of Mines. 1979. Mineral industry surveys, phosphate rock - 1978. Washington, D.C. 6 p.

Table 2. Phosphate trade - U.S. and world.

	World			U.S.	
Year	Total consumption[1]	Total trade[1]	Trade as % of consumption	Total trade[1]	Trade as % of world trade
1962	10,578	1,275	12	257	20
1963	11,311	1,328	12	248	19
1964	12,675	1,560	12	363	23
1965	13,955	1,683	12	392	23
1966	14,949	1,802	12	400	22
1967	16,111	2,049	13	713	35
1968	16,957	2,650	16	1,039	39
1969	18,175	2,554	14	902	35
1970	18,818	2,634	14	767	29
1971	19,844	2,630	13	815	31
1972	21,096	3,343	16	999	30
1973	22,440	3,891	17	1,264	32
1974	24,114	4,117	17	1,347	33
1975	22,653	4,151	18	1,498	36
1976	24,129	3,799	16	1,974	52
1977	26,479	4,337	16	2,268	52

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[1] 1,000 metric tons of P_2O_5

Source: Harre, E.A. and H.A. Handley. 1978. World fertilizer trade and the U.S. market outlook. In Situation 78, TVA Fertilizer Conference. National Fertilizer Development Center, Bulletin Y-131, Muscle Shoals, Alabama, p. 17-24.

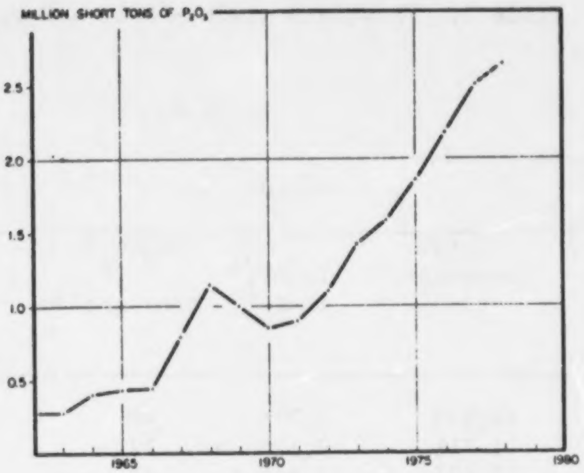

Figure 1. U.S. phosphate fertilizer exports.

Source: Harre, E.A. and Hazel A. Handley. 1978. World fertilizer trade and the U.S. market outlook, Situation 78, TVA Fertilizer Conference, August 15-16, 1978, St. Louis, Missouri. Bulletin Y-131. National Fertilizer Development Center, Muscle Shoals AL, 83 p.

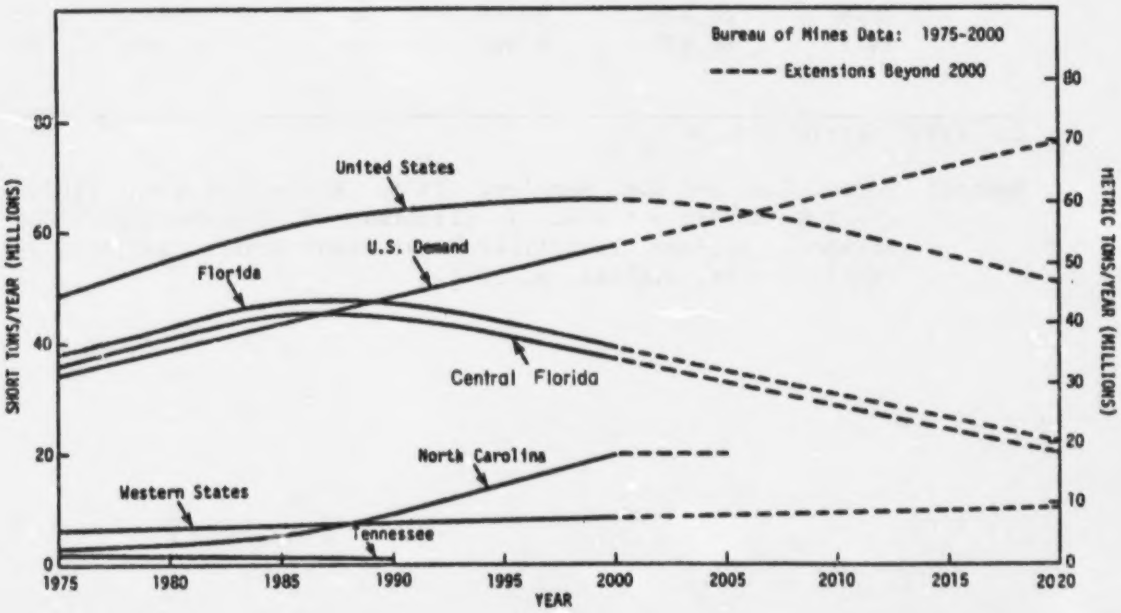

Figure 2. Phosphate rock supply - demand projections.

Source: Adapted from Stowasser, W.F. 1977a. Phosphate rock, the present and future supply and demand. Letter from U.S. Bureau of Mines to R.E. McNeill, USEPA, Region IV, February 18 in USEPA 1978b.

Table 3. Marketable production of phosphate rock in the United States, by region. (1000 metric tons and 1000 dollars)

	Rock	P_2O_5 Content	$Value
1977:			
Fla. & N. Carolina	40,575	12,679	718,393
Tennessee	1,747	442	14,253
Western States (1)	4,934	1,440	89,011
Total	47,256	14,561	821,657
1978:			
Fla. & N. Carolina	43,258	13,421	817,165
Tennessee	1,709	442	14,047
Western States (1)	5,070	1,469	97,608
Total	50,037	15,332	928,820

(1) Includes Alabama, California, Missouri, Montana, Utah, and Wyoming.

Source: U.S. Department of the Interior, Bureau of Mines. 1979. Mineral industry surveys, phosphate rock - 1978. Washington, D.C. 6 p.

Projections of United States production and consumption (Figure 2) of phosphate rock indicate that Tennessee production* will terminate around 1990. North Carolina production is expected to grow slowly through 1985 and then increase rapidly to a maximum mining rate of 20 million tons by 2000. This will occur as the Florida production rate is expected to reach a plateau of 48 million tons between 1985 and 1990 and then to decline as higher grade ores play out and production turns to lower grades. The western states' production is expected to increase slowly and continue steadily at approximately 8 million tons per year (USDI 1977). It seems likely that the United States will become a net importer of phosphate rock early in the 21st century.

1.3 PROCESSES

1.3.1 Background Information

1.3.1.1 The Development of Modern Fertilizers - Historical Perspective

The use of fertilizers has from early on been closely interrelated for the three primary plant nutrients - nitrogen, phosphorus, and potash. In 1840, Justus Liebig published results of his investigations into the elements plants need as nutrients, and laid the foundations of fertilizer science. Liebig identified ammonia (as ammonical liquor from coal gas, treated with gypsum), potash (from wood ash), and phosphorus and lime (from the treatment of ground bones with sulfuric acid), as well as other elements beneficial to plants. Liebig also described the ability of superphosphate to fix ammonia (superphosphate is the product of treating phosphate rock with sulfuric acid). By 1853, 14 firms in England, one in Austria, and three in the United States were producing "superphosphate of lime" by acidulation of bone meal (Russel et al. 1977). The search for other sources of phosphorus, as bones became an undependable supplier, led eventually to phosphate rock deposits, but superphosphate remained the dominant P fertilizer for more than 100 years.

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*Tennessee production is used for "furnace grade" phosphoric acid and elemental phosphorus and does not figure in as fertilizer production.

The United States Government established ammonia plant facilities and laboratories at Muscle Shoals, Alabama, in 1918 to produce synthetic ammonia needed in the World War. In 1933, the TVA was established as a regional resource development agency. TVA's mandate included the national responsibility for improving fertilizer manufacture and use through research, development, and education programs. During World War II, the ammonium nitrate was made available for fertilizer use, and TVA intensified development of other fertilizer materials, including improved phosphate fertilizers. Because of its role in education, through its National Fertilizer Development Center, TVA has been a catalyst in developing both new fertilizer materials and processes, and the markets and demands to utlize them. The Fertilizer Institute (TFI), based in Washington, D.C. has been active as a forum for discussion and dissemination of industry views and technical developments, and has recently become involved in symposia on environmental regulations and pollution control technology.

1.3.1.2 Phosphate Rock Mining and Processing

The phosphate mining industry is not included in the subject matter of this document. Since most phosphate rock mined, however, is used for production of fertilizer materials, most mining operations include phosphate fertilizer processing in their corporate activities. For example, of 34 major phosphate industry operations in the large Central Florida District, 18 perform processing of phosphate fertilizer or animal feed grade products (USEPA 1978b). Examined by company organization, the vertical integration is even more apparent. Many of the mining/beneficiation operations are owned by one parent company which may hold as many as three mining operations dedicated largely to supplying feedstocks for one or more processing plants of the same parent company. Mining and processing are briefly described below to assist the reader in distinguishing between the mining and manufacturing functions in an integrated facility.

After any prospecting and mining claims are complete, the mining operation concentrates on matrix or ore extraction and beneficiation of the ore. Figure 3 is a map showing the locations of the major phosphate deposits in the United States. Ore is actually mined in only four areas - Florida, North Carolina, Tennessee, and several western contiguous states.

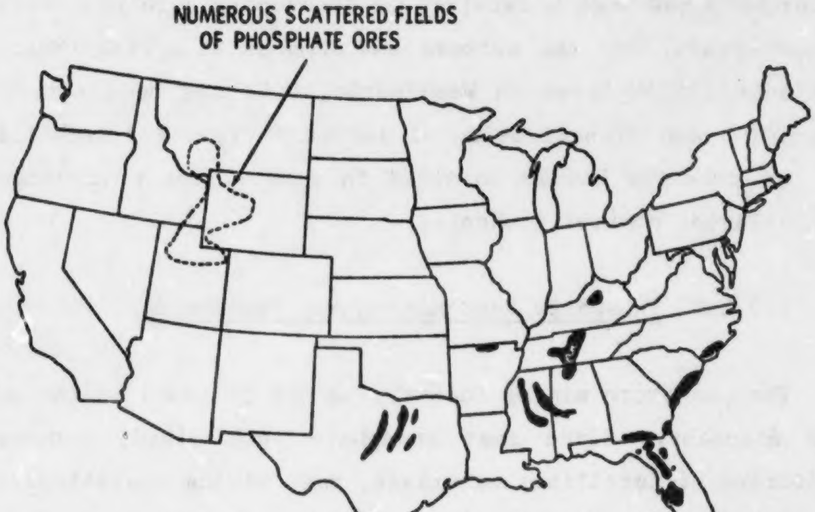

NUMEROUS SCATTERED FIELDS
OF PHOSPHATE ORES

Figure 3. Location of major phosphate rock deposits in the United States.

Source: Stowasser, W.F. 1977. Phosphate - 1977. Publication No. MCP-2, U.S. Department of Interior, Bureau of Mines, Washington, D.C., 18 p. in USEPA 1979a.

Extraction of the matrix or ore is done by different processes depending on the location and characteristics of the deposits. In Florida, which accounts for roughly 78% of the United States production of phosphate rock, deposits are alluvial. The phosphate-rich beds are a loosely consolidated conglomerate of phosphate pebbles and clays, known as matrix. The thin overburden deposits are unconsolidated sediments. Mining is conducted by stripping overburden from the matrix desposits by use of electrically driven "walking draglines" equipped with buckets of 20 to 65 cubic yard capacities and booms of 165 to 275 feet (USEPA 1978b). In successive moves of the draglines, matrix is removed and spoil from succeeding cuts is sidecast. As the ore is removed it is stacked in a sluice pit where hydraulic monitors (high-pressure water guns) slurry the ore into pumps for transport by pipeline to the washing plant (USEPA 1978b). One recent alternative is to remove oversize material near the mine pit and move dewatered and deslimed (clay removed) matrix by overland conveyors to the washing plant (Timberlake 1978).

In North Carolina the process is basically the same. The North Carolina deposits occur in interbedded phosphatic clays, limestones, and sands (USEPA 1971) Hydraulic sluicing and transport are also used in North Carolina where, as in Florida, level terrain and excellent pumping characteristics make these methods feasible.

In Tennessee, the high grade brown rock deposits are a weathered phosphatic limestone that occurs in a north-south belt across the state (Figure 3). Deposits are concentrated in small pockets of phosphate sands surrounded by silica sands. Mining is done by open pit methods. In Tennessee and also the western states, however, overburden is removed well in advance of actual mining operations (USEPA 1974a). Draglines and small power shovels are used to mine the phosphate sand, which is hauled by truck or rail to the processing plant.

In the western United States, phosphate deposits are mined in Idaho, Montana, Wyoming, and Utah, and account for 14% of United States production (Harre 1976). Western deposits are "hard rock" (consolidated) layers, with degree of hardness generally decreasing the farther north is the location. Conventional earth moving equipment is used to remove 5 to 50 feet of overburden. In Utah, the hard rock must be blasted with dynamite. In softer rock areas, "rippers" are used, which are toothed machines that gouge and break the rock from the surface. In Montana, two small underground mines are operated, using the room-and-pillar method, which is a kind of underground quarrying. Western rock is usually transported by rail to processing plants.

Beneficiation is the upgrading of the ore by application of processes to the mined matrix or ore to remove inert materials (such as silica sand) or extremely fine materials that cannot be economically separted. Florida and North Carolina beneficiation processes vary from plant to plant, depending on grade, size, and ratio of pebbles to fines. A generalized procedure starts with washing. The matrix slurry (20 to 50% solids) is passed through a series of screens, mills, and washers which break down the matrix to separate phosphate-bearing pebbles from sand and clays. Coarse screening obtains a first fraction of oversize phosphate ore. Further processing of the remaining matrix is done by cyclones to remove very fine sands and colloidal size materials. These are pumped to settling ponds and the remaining fraction undergoes a series of flotations (with tailings going to settling ponds) and finally the ore is dried. Some ore is ground and stored in silos, from which it is transferred to railroad hopper cars for transport (USEPA 1978e).

Tennessee ores are beneficiated by a similar process, except that all water is added at the beneficiation plant since matrix is received dry, and cyclones are operated in a water medium rather than air. A further step for most Tennessee ore is nodulizing in kilns, which prepares the ore for use in electric arc furnaces for production of elemental phosphorus (USEPA 1978d).

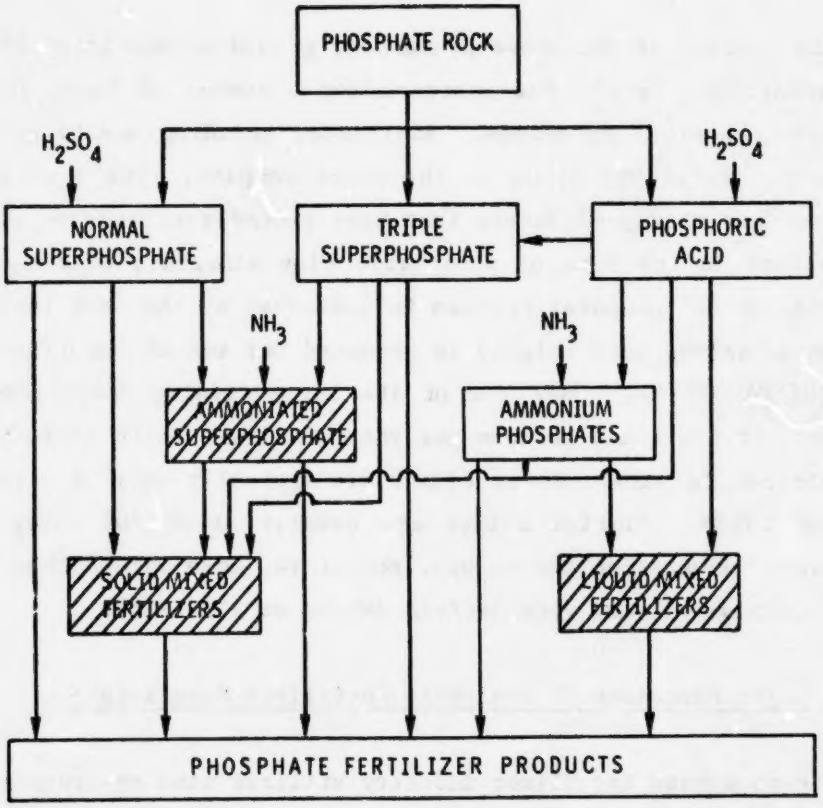
Western ore beneficiation starts with crushing and/or scrubbing. Subsequent sizing is done by further crushing, grinding, and size classification. Very fine and colloidal size materials are discharged to a slime pond or thickened for storage as a solid waste. The product is dried or may be calcined before shipment as a product.

Calcining is an operation done on some phosphate rock which is high in organic content or which will be used in processes requiring higher phosphate content. The rock is subjected to temperatures of 650-975 C (1200-1800 F) in rotary drum calcining units (USEPA 1978b). Organics are destroyed and tramp iron materials are removed magnetically. Because of the high energy demands of calcining, it is not done as routinely as it was in the past. Alternate methods can be used in some cases to remove impurities in later processes.

The product of the above processes, ground beneficiated phosphate rock or concentrate, is the raw material for a number of basic fertilizer and phosphorus chemical processes. Additional grinding may be performed after transport, or farther along in the plant complex. The beneficiation process produces slurry effluents that have caused notorious pollution problems in the past in the form of phosphatic clay slurries, or slime ponds. The magnitude of the disposal problem is indicated by the fact that approximately one ton of slimes (dry weight) is produced per ton of beneficated phosphate rock (USEPA 1977b). Just one of the larger mining operations in Florida produces 111.4 billion gallons per year of slimes, with up to 45% by weight -0.5 microns in size. These slimes are typically only 5% solids by weight (Hocking 1978). Florida slimes are usually about 70% water after 15 or more years' dewatering and occupy, therefore, more volume than the original matrix from which they were derived (White et al. 1978).

1.3.2 Major Processes of Phosphate Fertilizer Manufacture

The phosphate fertilizer industry utilizes nine separate processes, as discussed in Section 1.1. Figure 4 shows the relationships of basic, intermediate, and final product materials involved in phosphate-containing fertilizers. The two important basic processes are sulfuric acid (H_2SO_4) production and wet process phosphoric acid production. Sulfuric acid is produced and reacted with prepared phosphate rock to form either NSP or wet process phosphoric acid. NSP is used primarily as a direct application material or as a constituent in dry blended fertilizers.


PHOSPHATE ROCK
H_2SO_4
H_2SO_4
NORMAL SUPERPHOSPHATE
TRIPLE SUPERPHOSPHATE
PHOSPHORIC ACID
NH_3
NH_3
AMMONIATED SUPERPHOSPHATE
AMMONIUM PHOSPHATES
SOLID MIXED FERTILIZERS
LIQUID MIXED FERTILIZERS
PHOSPHATE FERTILIZER PRODUCTS

▨ **Products not included in the phosphate fertilizer subcategory**

Figure 4. Schematic diagram of phosphate fertilizer industry.

Source: Adapted from U.S. Environmental Protection Agency. 1971. Inorganic fertilizer and phosphate mining industries, Water pollution and control. Prepared by Battelle Memorial Institute, Richland WA, 226 p. in USEPA 1979a.

Wet process phosphoric acid is concentrated and clarified to product strength and is used to produce triple superphosphate or mono- or diammonium phosphate. Alternately, wet process phosphoric acid can be further concentrated and impurities removed to form superphosphoric acid (SPA). Wet process phosphoric acid is also used in production of blend fertilizer products or sold to other industrial users. The concentration of wet process phosphoric acid to form SPA is a process not specifically included in the phosphate fertilizer effluent guidelines Development Document (USEPA 1974a). Because of specialized operations and problems, however, and because the process is done only at plants also producing phosphoric acid (utilizing common waste streams, utilities, and pollution controls), a description of the superphosphoric acid manufacturing process is included.

In Figure 4, the product blocks with hatching represent mixed or blend fertilizers which are not covered in these Guidelines. The ammonium phosphates are technically mixed fertilizers because they contain more than one of the basic plant nutrients, but they were included in the subcategorization for phosphate fertilizer manufacture (and in this document) because they are normally produced in the same facilities as basic fertilizer materials and contribute to the same waste streams (By telephone, Dr. Elwood Martin, USEPA, January 26, 1979).

The phosphate fertilizer industry is remarkable for the degree of integration maintained among the processes at a typical installation. Consequently, the majority of the United States production is carried on at plant complexes, and the wastewater and gaseous effluents have largely been channeled into combined streams with common treatment systems to the extent this is feasible, or unless contaminants from certain processes may produce conditions more costly to treat at a later point.

The integrated character of the industry can be appreciated with reference to Table 4. The table shows that of the 114 plants in operation (in 1976) over 70% produce one type of phosphate fertilizer material only, and less than 30% of the plants consist of multiunit operations. Those relatively few multiunit plants, however, account for more than 80% of the total volume of phosphate fertilizers (USEPA 1979a).

Table 4. Description of phosphate fertilizer complexes in the United States by unit operations.

Unit operations at plant site	Number of plants with this combination	Percent of total
WPPA only	7	6.1
NSP only	54	47.3
DAP only	20	17.4
WPPA, SPA	3	2.6
WPPA, NSP	1	0.9
WPPA, TSP	2	1.8
WPPA, DAP	10	8.8
NSP, TSP	1	0.9
WPPA, TSP, DAP	6	5.3
WPPA, SPA, DAP	2	1.8
WPPA, NSP, TSP	1	0.9
NSP, TSP, DAP	1	0.9
WPPA, SPA, TSP, DAP	4	3.5
WPPA, NSP, TSP, DAP	1	0.9
SPA, NSP, TSP, DAP	1	0.9
TOTAL	114	100

WPPA - Wet process phosphoric acid.
DAP - Diammonium phosphate.
NSP - Normal superphosphate.
SPA - Superphosphoric acid.
TSP - Triple superphosphate.

Source: US Environmental Protection Agency. 1979a. Source assessment: Phosphate fertilizer industry. Office of Research and Development, Washington, DC. Prepared by Nyers, J.M., G.D. Rawlings, E.A. Mullen, C.M. Moscowitz, and R.B. Reznik, Monsanto Corp., Dayton OH, 201 p.

In addition, although effluent guidelines apply to both single unit and multi-unit operations, those standards were promulgated cognizant of the operating procedures of the integrated complexes, in which contaminated water is typically used for all processes where presence of contaminants is not critical. For example, contaminated water is recycled for use in wet scrubbers, to rinse precipitates from filters, and to supply barometric condensers and heat exchangers (USEPA 1979a, USEPA 1974a). Each time the water is recycled, the levels of contaminants are increased, but a key point applicable to the process descriptions in the sections which follow is that typically this contaminated wastewater is not discharged from the complex. It is a process effluent or wastestream, but it is not a regularly discharged effluent. The Source Assessment conducted by Monsanto researchers during 1976 and 1977 (USEPA 1979a) revealed that only approximately 8% of all phosphate fertilizer plants still routinely discharge wastewater.

These figures do not reflect, however, that most existing plants still have the need to discharge water for certain periods of time during most years. Because the recycled water systems are usually a series of large outdoor ponds, extended heavy rains necessitate discharge of excess accumulated water. Excess water can also develop due to occasional miscalculations or misadjustments of chemical reaction processes, resulting in errors in water management plans. In general, plant operators attempt to avoid such discharge events due to USEPA and state requirements for pretreatment of discharged wastewaters, at additional cost to the operators. Further wastewaters from uses which are not involved in production processes (non-process wastewaters) can be discharged continuously and in many cases are kept separate from process wastewaters to effect economies in treatment costs.

1.3.2.1 Sulfuric Acid Production

Production of phosphoric acid by the wet process requires almost one ton of sulfur (as sulfuric acid) for each ton of P_2O_5 produced. In the United States virtually all sulfuric acid is produced by the contact process, which represented 99.3% of total production in 1971 and had increased to 99.8% in 1976 (USEPA 1978a). Since New Source Performance Standards (NSPS) for SO_2 were promulgated in 1971, the "double" or "dual" absorption process has become the system of choice because of its efficacy as a combined process option/emissions control system that meets the NSPS for SO_2.

All contact sulfuric acid manufacturing processes incorporate three basic operations:

(1) burning of sulfur or sulfur-bearing feedstocks to form SO_2;
(2) catalytic oxidation of SO_2 to SO_3; and
(3) absorption of SO_3 in a strong acid stream.

The least complicated systems burn elemental sulfur. Additional operations are required to remove moisture, organics, and particulates prior to catalysis and absorption when feedstocks such as spent acid and acid sludge are used (USEPA 1978a).

Elemental Sulfur Burning Sulfuric Acid Production - Single Absorption

Elemental sulfur is the feedstock for sulfur burning contact process acid for about 68% of total U.S. production (USEPA 1978a) and for sulfuric acid produced at fertilizer plants for captive use it is the only feedstock in use (USEPA 1977b, USEPA 1978b). The process is represented by the schematic flow diagram, Figure 5.

In this process molten elemental sulfur is filtered and sprayed into a dry air stream inside a furnace. Combustion air has been predried by passing it through a drying tower containing 93.2-99% sulfuric acid. The high furnace temperature auto-ignites the sulfur and oxidizes it to form SO_2. This exothermic

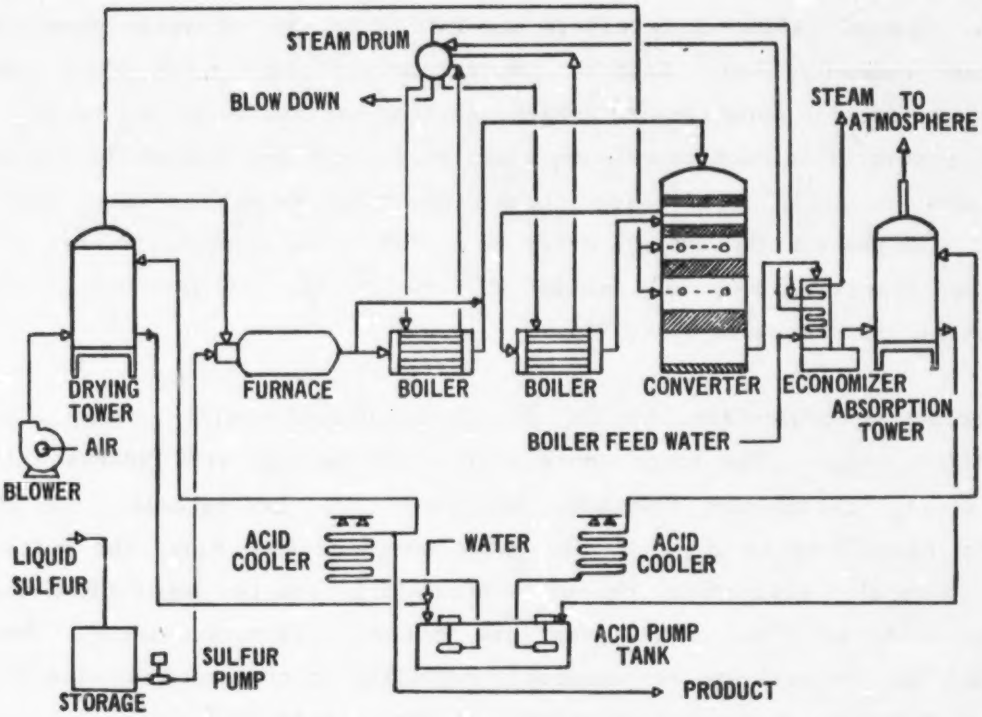

STEAM DRUM
BLOW DOWN
STEAM
TO ATMOSPHERE
DRYING TOWER
FURNACE
BOILER
BOILER
CONVERTER
ECONOMIZER
ABSORPTION TOWER
BOILER FEED WATER
AIR
BLOWER
LIQUID SULFUR
ACID COOLER
WATER
ACID COOLER
ACID PUMP TANK
SULFUR PUMP
STORAGE
PRODUCT

Figure 5. Contact-process sulfuric acid plant burning elemental sulfur - single absorption.

Source: U.S. Environmental Protection Agency. 1971a. Background information for proposed new source performance standards. Office of Air Programs, Research Triangle Park NC in USEPA 1978a.

reaction releases large amounts of heat. The mixture of SO_2 and excess combustion air (8-11% SO_2 by volume) reaches temperatures of 980-1140 C (1800-2000 F) as it leaves the furnace. It is cooled by being routed through a boiler, where steam is generated and the temperature of the SO_2-air mixture is reduced to an optimum temperature for chemical conversion of the SO_2 to SO_3.

The cooled SO_2 gas, together with predried air, then enters the solid catalyst converter where it is converted to SO_3 in a series of three or four steps. Several different catalysts are available, but vanadium pentoxide is the most commonly used. Each of the conversion steps takes place under a different reaction condition to achieve optimum conversion of SO_2 to SO_3. The gas temperatures in each conversion stage rise until equilibrium is approached; the gases are cooled after each intermediate stage as well as after the final stage. The gas exiting the converter is cooled in an economizer (heat exchanger) to temperatures between 230 and 260 C (450-500 F). At this stage SO_2-SO_3 conversion efficiency is about 98%.

Following conversion the SO_3 gas is circulated upward through a packed absorption tower. The tower contains ceramic packing with 98-99% sulfuric acid (H_2SO_4) circulating downward, counter to the gas current. The SO_3 is readily hydrolized to H_2SO_4 by the water in the acid. Since the hydrolysis reaction is also exothermic, the acid circulating from the tower flows through cooling coils and then to the pump tank whence it is recirculated. The acid strength and temperature are carefully regulated to prevent excessive SO_3 release. Normally, absorption efficiency is essentially 100%.

The pump tank acts as a reservoir for process sulfuric acid. The enriched 98-99% acid enters the pump tank, and a portion is recycled through the absorption tower. Also a portion of the acid is cycled to the air drying tower. In this operation the 98-99% acid is first diluted to approximately 93% and circulated through the drying tower, counter-current to the upward circulating air. Moisture in the air is absorbed by the acid (slightly diluting it further) and the dry air enters the furnace. The 93% diluted acid returns to the pump tank for mixing with the 98-99% acid flowing in from the absorption tower. Product acid is the excess over drying tower and absorption tower recycle requirements. It is diluted with water to the desired concentration (normally 93%) and is pumped to storage as the pump tank is monitored and maintained at a constant level.

The basic requirements and functions of sulfuric acid production are summarized in the following table:

Table 5. Sulfuric acid manufacture from elemental sulfur.

Input Materials

- Sulfur
- Air
- Water (make-up water)

Utilities

- Cooling water (process water)
- Electrical energy
- Filter acid
- Steam (production)

Waste Streams

- Tail gas (containing SO_2 and acid mist)
- Cooling water blowdown
- Boiler blowdown

Product

- Sulfuric acid, which may be used for

  --normal superphosphate processing
  --wet process phosphoric acid production
  --ammonium phosphate processing
  --ammoniation/granulation/drying
  --out of plant sales

Several terms introduced above are used repeatedly in industrial process descriptions:

Make-up water is feed water that is of acceptable quality for utilization within a process, including use as a raw material.

Process water is any water which, during the manufacturing process, comes into contact with any raw material, intermediate, product, or by-product, or with gas or liquid that has accumulated such constituents.

Blowdown is the purge from the system of a small portion of the concentrated water (from a boiler or recirculating process stream) in order to maintain the maximum level of dissolved and suspended solids in the system.

Tail gas is the accumulated captive gaseous waste stream at the end of a process.

Elemental Sulfur Burning Sulfuric Acid Production - Double Absorption

The double absorption process, which was used partially as the rationale for the SO_2 NSPS has become the control system of choice by sulfuric acid manufacturers since the NSPS were promulgated in 1971. Because it is a very widely utilized process option, rather than an add-on emission control system such as an ammonia scrubber, it is described at this point and is referenced in the Section 3.2 discussion of pollution control technology.

Figure 6 is a process flow diagram which incorporates the double absorption system. The essential feature that differentiates it from the single absorption process is the addition of the second absorption tower. The second tower is installed at a point intermediate between the first and final SO_2-to-SO_3 catalytic conversion steps. This second absorption process permits the achievement of a greater conversion of SO_2 to SO_3 and significantly reduces the quantity of SO_2 in the effluent gas stream. Double absorption plants achieve SO_2 conversion efficiencies of 99.5+% as compared with approximately 98% efficiencies for single absorption plants. Wastewater effluents are the same for either process in regard to quantities and contaminant levels.

In either process option, single or double absorption, the cooling tower closed loop and the boiler for waste heat removal are standard systems. Closed loop cooling systems function with forced air and water circulation to effect water cooling by evaporation. Evaporation acts to concentrate the natural water impurities as well as the treatment chemicals required to inhibit scale growth, corrosion, and bacteria growth. Such cooling systems require routine blowdown to maintain impurities at an acceptable operating level. The blowdown quantity will vary from plant to plant and is dependent upon the cooling water circulation system.

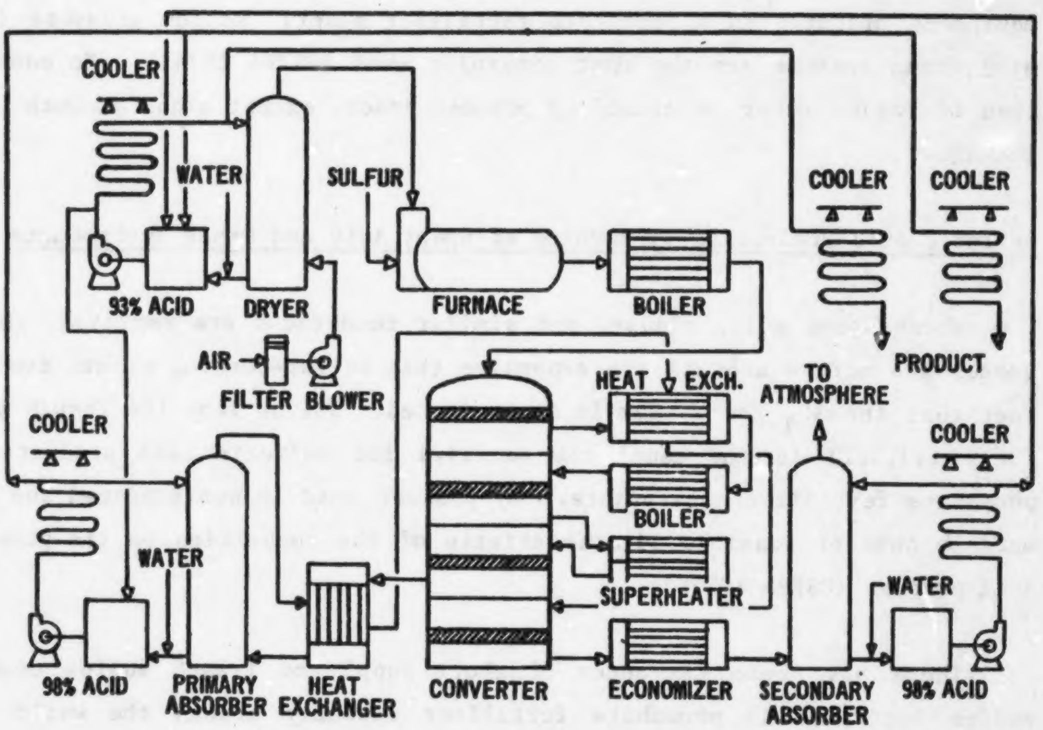

COOLER
WATER
SULFUR
COOLER
COOLER
93% ACID
DRYER
FURNACE
BOILER
AIR
FILTER
BLOWER
PRODUCT
HEAT EXCH.
TO ATMOSPHERE
COOLER
COOLER
BOILER
WATER
SUPERHEATER
WATER
98% ACID
PRIMARY ABSORBER
HEAT EXCHANGER
CONVERTER
ECONOMIZER
SECONDARY ABSORBER
98% ACID

Figure 6. Dual absorption sulfuric acid plant flow diagram.

Source: U.S. Environmental Protection Agency. 1971a. Background information for proposed new source performance standards. Office of Air Programs, Research Triange Park NC in USEPA 1978a.

"The type of process equipment being cooled normally has no bearing on the effluent quality. Cooling is by an indirect (no process liquid contact) means. The only cooling water contamination from process liquids is through mechanical leaks in heat exchanger equipment. Such contamination does periodically occur and continuous monitoring equipment is used to detect such equipment failures" (USEPA 1974a).

The boiler in the sulfuric acid process is the only steam generation equipment operated in a phosphate fertilizer plant. Medium pressure (9.5-52 atm) steam systems are the most generally used (USEPA 1974a). No contamination of boiler water is caused by process gases, except minor amounts through leakage.

Sulfuric Acid Production by Burning of Spent Acid and Other By-Products

Where spent acid, sludge, and similar feedstocks are employed, the processes are more elaborate and expensive than sulfur-burning plants due to the fact that the SO_2 gas stream is contaminated. Sulfur from the Frasch process (Sec. 1.3.3.1) is the usual raw material for sulfuric acid production for phosphate fertilizer manufacture. By-product acid is not produced and seldom used because of possible adverse effects of the impurities on the phosphoric acid process (USEPA 1977b).

There have been instances of short supply of Frasch sulfur caused by sudden increases in phosphate fertilizer capacity around the world (Slack 1968) but U.S. producers generally purchase sulfuric acid when necessary to supplement in-plant production. Normally, other types of sulfur feedstock are not utilized by the phosphate fertilizer industry.

1.3.2.2. Phosphate Rock Processing - Crushing, Grinding, and Screening

Beneficiated phosphate rock usually requires additional processing to reduce the ore to the particle size range for optimal phosphoric acid production. Crushing and grinding are done with ball, ring-roller, or bowl mills, and with hammer mills. The first three are rotational mills where the feed material is crushed and ground (respectively) by:

(1) crushing among steel balls in a rotating compartment (a type of "tumbling mill");

(2) crushing between a grinding ring and two or more rollers which rotate orbitally around the outer surface of the ring;

(3) crushing between rotating rollers and the inner surface of a grinding ring within a bowl shaped chamber.

Hammer mills operate by crushing material by impact and grinding. The hammers (massive protrusions in a variety of shapes) project from a rotating shaft which rotates in a housing containing grinding plates or liners (Perry 1969).

After the rock enters the mill system, flow through sizing and reclamation circuits is by pneumatic means when dry grinding is performed. Air is constantly exhausted from the mill system to prevent precipitation of moisture released from the fractured rock and entrained rock particles are removed usually by bag type filters before the air is vented to the atmosphere. Figure 7 illustrates the process flow for rock grinding.

An alternative to this process is wet grinding of phosphate rock. It was in the period of 1973-1975 that the first commercial installations were developed for use in conjunction with wet process phosphoric acid production. The major objective was to reduce energy requirements by eliminiating drying of the rock. Wet grinding also eliminates the need for dry storage of incoming rock and greatly reduces problems in collection and handling of dust. Wet grinding is accomplished with the addition of small amounts of water to the feed, and flow of ground rock to the phosphoric acid process is in the form of a slurry. The wet grinding process is operating well in several installations and is considered a promising recent technological advance. At one new source plant the operator is planning to utilize wet phosphate rock without any grinding (USEPA 1978p). In that instance at the proposed Swift Creek Chemical Complex in Hamilton County, Florida, the operator will utilize phosphate ore from the Hawthorn geologic formation, which occurs in sand-size particles unlike the pebble-size ore in the central Florida Bone Valley formation and the massive hard rock ores of western states.

No wastewater effluents are produced by either dry or wet grinding. Only small amounts of water (Figure 7) are utilized for indirect cooling of lubricating oil and mechanical equipment. Exact amounts utilized for cooling in wet grinding were not determined, but would also be very minor. The water added to phosphate rock for wet grinding is incorporated into the process reactants. The required basic materials for the phosphate rock grinding, crushing, and screening process are listed in the following summary:

Table 6. Phosphate rock crushing, grinding, and screening.

Input Materials

- Phosphate rock, as mined for certain high grade ores, or beneficiated
- Air (not consumed; dry grinding only)
- Water (make-up water; wet grinding only)

Utilities

- Cooling water (process water)
- Electrical energy

Waste Streams

- Air (containing particulate phosphate rock)
- Cooling water (non-contaminated discharge; water has increased temperature only)

Product

- Ground phosphate rock (dry grinding)
- Ground phosphate rock slurry (wet grinding)

Since phosphate rock being ground is for reaction in a particular downstream process or, in the case of some high grade ores, for sale to other industries, the desired particle size varies according to ultimate use. For example, most wet-process phosphoric acid in the United States is produced from 35-mesh to 150-mesh particulate (0.4mm-0.09mm), the size of medium to very fine sand. Standard practice has been to grind to the very fine sand sizes to optimize chemical reaction of the phosphate rock. Energy is required whenever size reduction is used to achieve these sizes (some sizing is first accomplished by screening in the beneficiation process). Less energy is

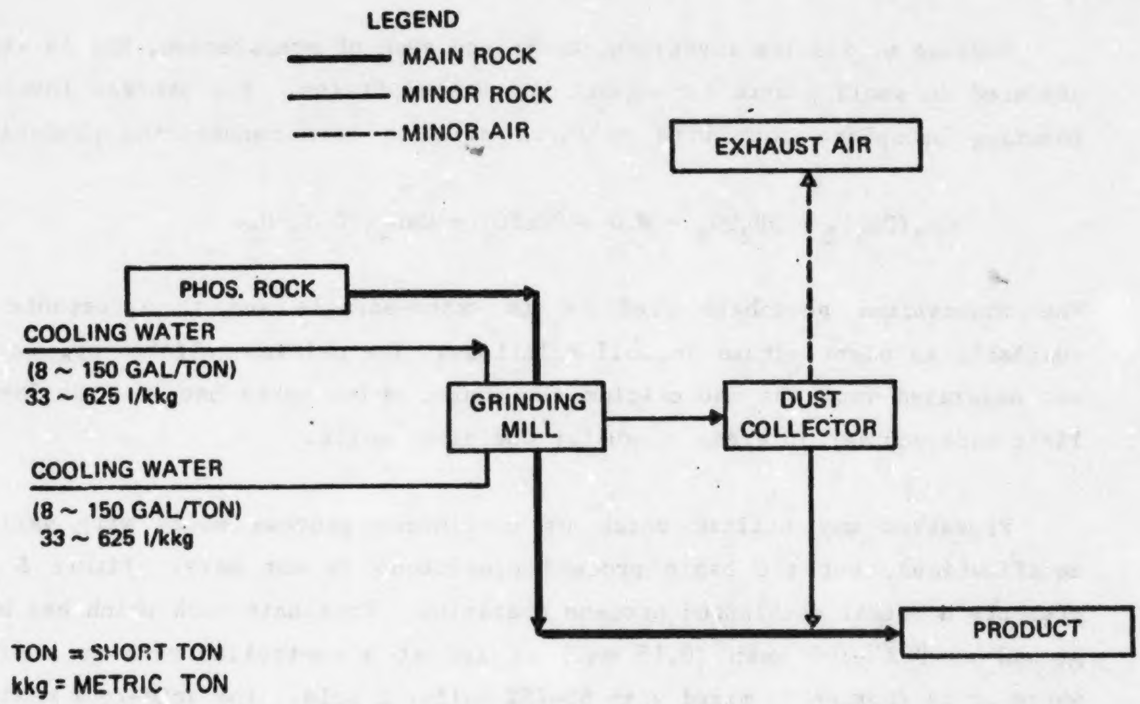

LEGEND
MAIN ROCK
MINOR ROCK
MINOR AIR
EXHAUST AIR
PHOS. ROCK
COOLING WATER
(8 ~ 150 GAL/TON)
33 ~ 625 l/kkg
GRINDING MILL
DUST COLLECTOR
COOLING WATER
(8 ~ 150 GAL/TON)
33 ~ 625 l/kkg
PRODUCT
TON = SHORT TON
kkg = METRIC TON

Figure 7. Rock grinding (flow rate per ton rock).

Source: Adapted from U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC, 168 p.

required when less grinding is required, and at least one process, the Kellogg-Lopker process (Anonymous 1972a), is in use in England which requires less grinding (90-95% -40 mesh). Depending on the phosphate rock source, some portion of this sizing is accomplished by screening alone. No United States plants are utilizing the Kellogg-Lopker process at this time.

1.3.2.3 Normal Superphosphate Production

Because of its low investment costs and ease of preparation, NSP is still produced in small plants throughout the United States. The process involves reacting phosphate rock with sulfuric acid to form monocalcium phosphate:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + H_2O \rightarrow 2CaSO_4 + CaH_4(PO_4)_2 \cdot H_2O$$

The monocalcium phosphate produced is water-soluble and the phosphate is available to plant uptake in soil solutions. The calcium sulfate (gypsum) is not separated from the monocalcium phosphate, which makes use of this fertilizer more popular in areas of sulfur deficient soils.

Processes may utilize batch or continuous process modes with various modifications, but the basic process operations do not vary. Figure 8 represents a normal continuous process operation. Phosphate rock which has been ground to 90% -100 mesh (0.15 mm.) is fed at a controlled rate to a mixer where it is thoroughly mixed with 65-75% sulfuric acid. The acid-rock mixture is a slurry which is discharged to a pug mill where additional mixing and reaction takes place. The reaction is very rapid and exothermic.

A pug mill consists of a horizontal cylindical or trough shaped chamber containing one or two rotating shafts fitted with short heavy paddles. The slurry is fed into one end of the mill and is both cut through and forced forward by the paddles until the slurry is discharged through an opening at the other end of the mill. Residence time in the pug mill for NSP production is two minutes or less.

From the mill the slurry discharges to a slow moving conveyor (continuous den) where the reaction continues and the slurry stiffens to a plastic mass.

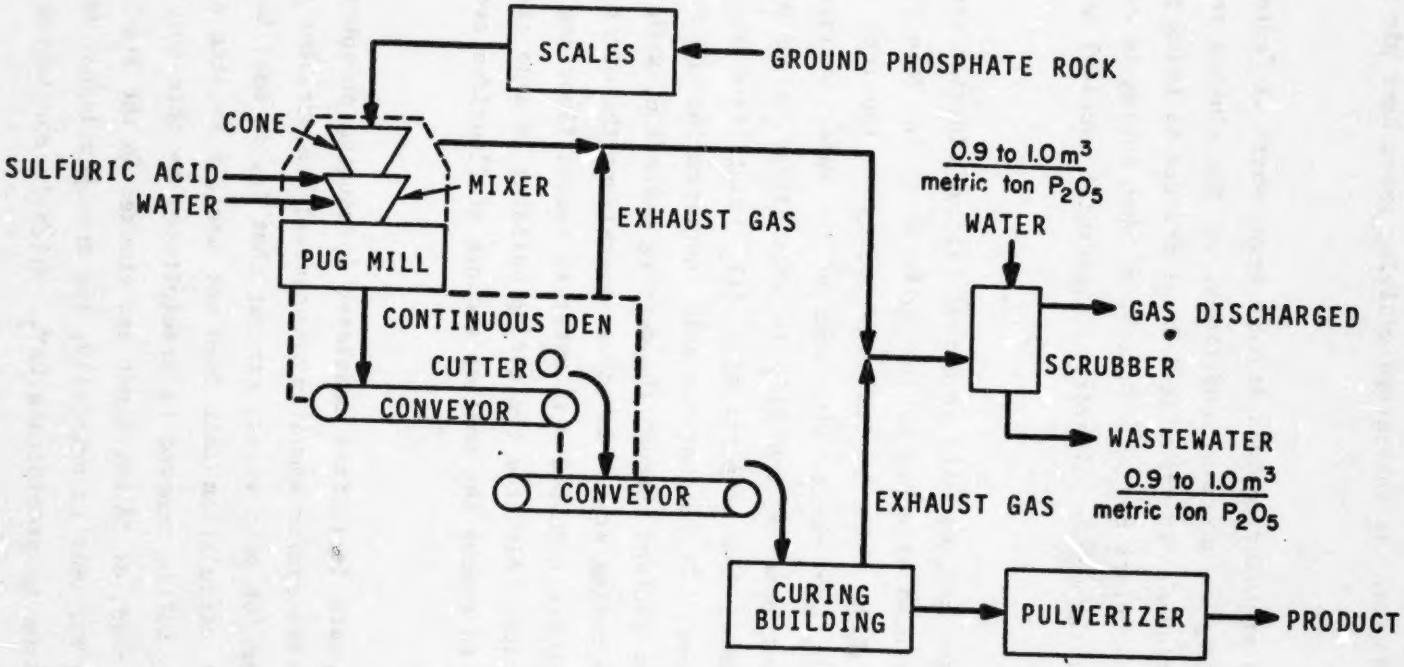

SCALES
GROUND PHOSPHATE ROCK
CONE
SULFURIC ACID
WATER
MIXER
PUG MILL
EXHAUST GAS
CONTINUOUS DEN
CUTTER
CONVEYOR
CONVEYOR
CURING BUILDING
PULVERIZER
PRODUCT
EXHAUST GAS
$\frac{0.9 \text{ to } 1.0 \text{ m}^3}{\text{metric ton } P_2O_5}$
WATER
SCRUBBER
GAS DISCHARGED
WASTEWATER
$\frac{0.9 \text{ to } 1.0 \text{ m}^3}{\text{metric ton } P_2O_5}$

Figure 8. Normal superphosphate flowsheet.

Source: Adapted from U.S. Environmental Protection Agency. 1971. Inorganic fertilizer and phosphate mining industries, Water pollution and control. Prepared by Battelle Memorial Institute, Richland WA, 226 p.

(In batch processes the den is internally stationary, with no conveyor). Den residence time varies from one to four hours. As the plastic mass leaves the conveyor it is cut into chunks. At this stage evolving gases have given it a honeycomb appearance.

The cut up product is transferred to a storage area, where it "cures" for two to six weeks, depending on process conditions, as the slowing reaction between rock and acid continues. If granulated final product is being produced granulation is usually done before curing. Otherwise, when curing is complete the solidified NSP is fed through a pulverizer (hammermill usually) where it is crushed and screened.

Returning to the mixer and pug mill reaction, calcium fluoride contained in the phosphate rock is also attacked by the sulfuric acid. This reaction forms hydrofluoric acid (HF), which reacts with silica in the rock to form SiF_4 plus water. This in turn reacts with some of the water to form fluosilicic acid (H_2SiF_6), but some of the SiF_4 is volatilized before reaction with water can take place. The proportion of SiF_4 volatilized depends on concentration of H_2SO_4 used. The higher the acid concentration the more SiF_4 is evolved. SiF_4 is also evolved through the denning operation, with a small amount forming during the curing step. In actual operations the mixer and den are enclosed and emissions are scrubbed with water to remove fluorides and any acid mist and dust particles. Air from the curing building is also circulated through the wet scrubber to remove the smaller amounts of fluorides evolved in that stage.

In integrated phosphate fertilizer complexes (producing phosphoric acid and/or triple superphosphate and/or ammonium phosphates) the scrubber uses the common contaminated water (or pond water) stream; that is, in most instances, a closed loop wastewater circulation that does not usually require discharge from the plant system. Solids removed or precipitated in this solution are contained in the gypsum pond, or filtered out and stacked on the premises. In smaller plants producing NSP only or primarily, the scrubber liquor is usually run into beds of limestone to precipitate CaF_2, which is considered to be a solid waste (USEPA 1979a).

The basic process constituents for NSP production are summarized below:

Table 7. Normal superphosphate production.

Input Materials

- Pulverized phosphate rock
- Sulfuric acid
- Water (make-up water to dilute sulfuric acid)

Utilities

- Electrical energy
- Scrubber water

Waste Streams

- Air (particulate phosphate rock, acid mist, fluorides)
- Water (process water) - the only process water involved is scrubber effluent
- Solids - CaF_2 and dust absorbed in scrubber effluent are precipitated or allowed to settle out in gypsum ponds

Product

- Normal superphosphate - generally sold as fertilizer or dry mixed with other fertilizer materials and sold as solid mixed fertilizer

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1.3.2.4 Wet Process Phosphoric Acid Production

Phosphoric acid is the most important intermediate manufactured by the phosphate fertilizer industry because it is a basic ingredient to every phosphate fertilizer product which the industry produces other than normal superphosphate and salable phosphate rock. Phosphoric acid can be produced by either the digestion of phosphate rock with a mineral acid (wet process) or by hydration of phosphorus with air in an electric furnace (thermal process). The acid produced by the thermal process, which requires considerable energy consumption, is known as furnace grade acid and is of higher purity than wet process acid. Furnace grade acid is used for animal feeds, detergents, fire retardant chemicals, and other industrial phosphorus products, but is no longer used to produce phosphate fertilizers (USEPA 1979a).

Wet process acid contains more impurities than does furnace grade acid, and is known as merchant grade phosphoric acid. All phosphate fertilizer production from phosphoric acid in the United States uses wet process acid. The wet process is based on reaction of phosphate rock with a suitable strong acid to produce phosphoric acid and an acid salt. The choice of strong acid depends on such factors as cost and availability, simplicity of operation, materials of construction and type of equipment required, and the waste streams and end products generated. In the United States, sulfuric acid is far and away the most widely used, but nitric and hydrochloric acid can also be used. In 1973 98.77% of all wet process phophoric acid utilized sulfuric acid acidulation, with 1.23% utilizing nitric acid and no plants using hydrochloric acid (USEPA 1974a). Current data on type of acid used for acidulating phosphate rock is not readily available, but no mention of commercial use of acids other than sulfuric has been noted in references since the surveys done for the USEPA Development Document (USEPA 1974a).

In general, nitric acid acidulation has been characterized by complex multi-stage processes, requiring use of additional mineral acids and organic solvents, with serious consequent corrosion problems. Furthermore, several additional stages involving costly cooling, crystallizing of dissolved calcium nitrate, and addition of additional reagents to precipitate calcium, results in typically viscous phosphoric acid of 27 to 35% P_2O_5. Alternatives to remove calcium cleanly require use of ammonia, which is itself an energy-consuming somewhat costly product to manufacture. The simplest of nitric acid acidulation processes utilizes ammoniation of the acidulated acid-rock solution to produce nitric phosphate, a fertilizer material, but the phosphoric acid is not obtained, having been present only in the solution, and some of the phosphate becomes tied up in calcium phosphate, which is not water soluble and therefore not useful as a fertilizer (Slack 1968). For such reasons, nitric acid acidulation is not widely used and has normally been employed only when nitric acid is a cheap or readily available coproduct in an industry. No further discussion of nitric acid acidulation is warranted in this Guidelines document.

Sulfuric Acid Acidulation of Phosphate Rock

The popular process of acidulation of phosphate rock with sulfuric acid has the advantage of quick formation of calcium sulfate dihydrate, or gypsum ($CaSO_4 \cdot 2H_2O$). All acidulation processes produce gaseous and liquid effluents which must be controlled, but disposal of the solid by-products formed poses the most cumbersome potential problem. 1.76 metric tons of phosphate rock concentrate (average 32% P_2O_5) and 1.53 metric tons of sulfuric acid (average 93% H_2SO_4) are reacted per metric ton of phosphoric acid produced (USEPA 1977b). Typically, 4.6 to 5.2 metric tons of gypsum by-product are formed per metric ton of phosphoric acid (USEPA 1979a). Nonetheless, as described in the discussion of nitric acid acidulation, the formation of a stable, filterable by-product which does not take significant amounts of phosphate ion out of the system is a distinct advantage.

Besides the dihydrate form, it is also possible with sulfuric acid digestion processes to precipitate calcium sulfate as the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) or the anhydrite ($CaSO_4$) form. The dihydrate process has offered basic advantages over the other two processes, such as less severe operating conditions, lower rates of corrosion, better filterability, and lower capital cost. Figure 9 shows the precipitation conditions for calcium sulfates in phosphoric acid.

A flowsheet typical of the dihydrate process is shown in Figure 10. Ground beneficiated or concentrated phosphate rock is fed continuously to a reaction system where it is mixed with sulfuric acid. The sulfuric acid is diluted, sometimes with contaminated process water, to a proper strength depending on the process design and on phosphate rock composition to ensure optimal dihydrate crystallization. Some commercial processes also recycle some dilute phosphoric acid into the reaction system. Older plants may have one or more digestion or attack tanks, but in more recent installations the the reaction system is a single large compartmented tank. In this attack vessel, the rock and acid react to form dihydrate (gypsum) and phosphoric acid according to the following reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O)$$

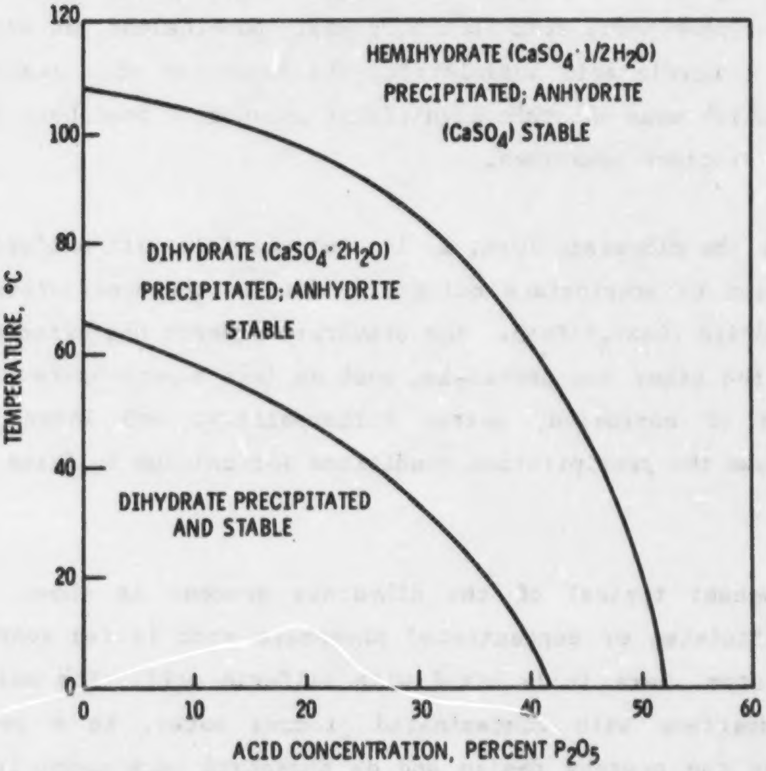

Figure 9. Precipitation and stability of calcium sulfates in phosphoric acid.

Source: Slack, A.V. 1967. Chemistry and technology of fertilizers. John Wiley & Sons, Inc., New York NY, p. 69-97 in USEPA 1979a.

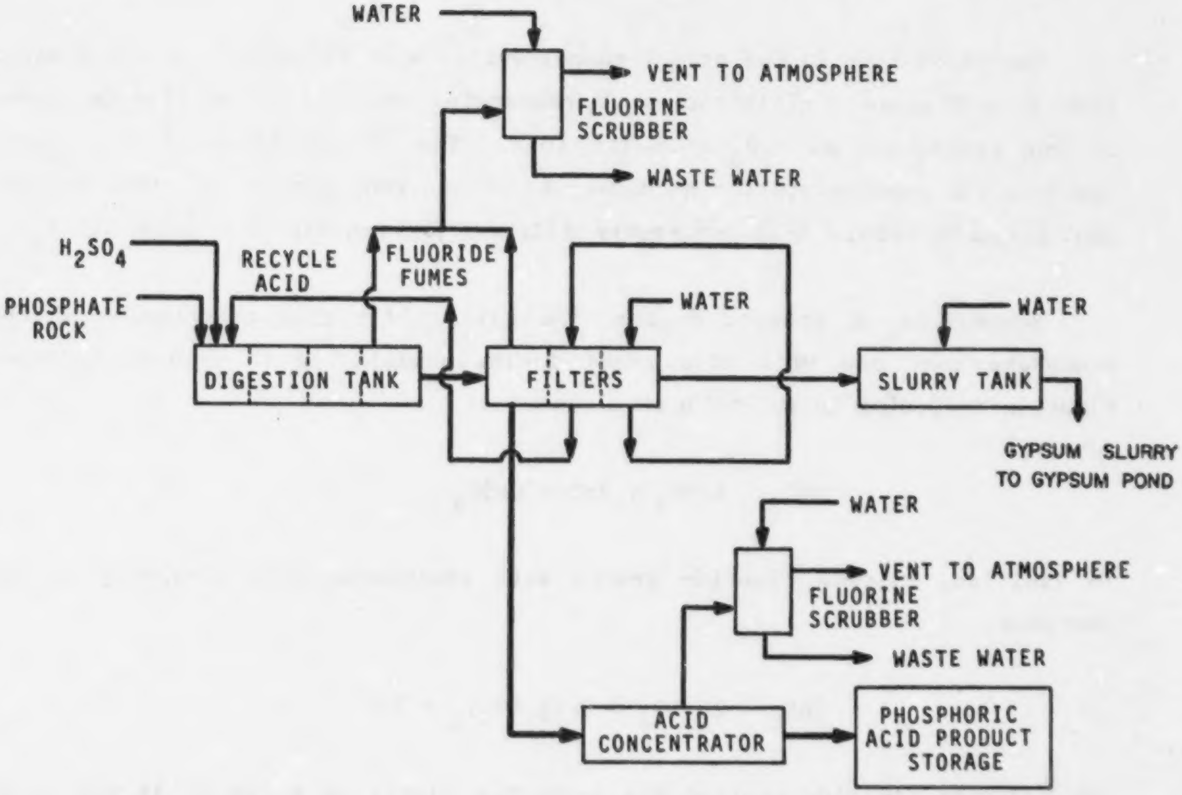
WATER
VENT TO ATMOSPHERE
FLUORINE SCRUBBER
WASTE WATER
H_2SO_4
RECYCLE ACID
FLUORIDE FUMES
PHOSPHATE ROCK
WATER
WATER
DIGESTION TANK
FILTERS
SLURRY TANK
GYPSUM SLURRY TO GYPSUM POND
WATER
VENT TO ATMOSPHERE
FLUORINE SCRUBBER
WASTE WATER
ACID CONCENTRATOR
PHOSPHORIC ACID PRODUCT STORAGE

Figure 10. Wet process phosphoric acid flowsheet.

Source: Adapted from U.S. Environmental Protection Agency. 1971. Inorganic fertilizer and phosphate mining industries, Water pollution and control. Prepared by Battelle Memorial Institute, Richland WA, 226 p.

To obtain complete reaction commercial processes mix or recirculate the rock-gypsum-acid slurry through the tank compartments. The temperature in the attack vessels is also controlled (usually at about 75 C) to ensure formation of dihydrate. The reaction is exothermic, with higher heats produced when more concentrated acids are used. Cooling water, vacuum coolers, air sparging (flowing air through a liquid) and dilution and cooling of the acid are techniques used to control process temperatures.

Retention time in the attack vessel varies with different process designs from 3 to 8 hours. Efficiencies of commercial systems are usually in excess of 96% extraction of P_2O_5 from the rock. The recirculation of the slurry controls the supersaturation necessary to attain good growth of gypsum crystals. The gypsum crystals must be easily filtered and retain a minimum of P_2O_5.

Regardless of process design, the calcium fluoride constituent of the phosphate rock ore will also react during acidulation to produce hydrogen fluoride according to the following reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

In addition, calcium fluoride reacts with phosphoric acid according to the reaction:

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF$$

The hydrogen fluoride evolved may leave the slurry as a gas or it can react with silica present in the phosphate rock:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

During the later acid concentration steps, fluosilicic acid (H_2SiF_6) in the phosphoric acid solution can dissociate by the following reaction:

$$H_2SiF_6 \rightarrow SiF_4 + 2HF$$

The fluoride products formed can all volatilize and are major emission species in the contaminated emission stream. All reaction systems include a system to pass evolved gases through wet scrubbers to remove fluorides, along with acid mists and particulates.

Each system design varies as to the number and location of agitators or recirculation mechanisms and in the locations and methods of phosphate rock and sulfuric acid points. In the United States, approximately 75% of all wet process reaction systems or "trains" use the Prayon or the Prayon/Dorr-Oliver systems. Figures 11 through 14 illustrate schematically four systems using different equipment, but the basic process and the resulting product and by-products are essentially the same.

The acid slurry in all systems flows from the digestor to a filter system where the gypsum solids are removed. A typical filter system yields two phosphoric acid streams:

- a 30-32% P_2O_5 product stream;
- an approximately 20% P_2O_5 content acid stream which recycles to the digestor.

Figures 15 and 16 illustrate the widely used tilting pan filtration system. Slurry is discharged onto the filter and the undiluted mother liquor (product) is collected and pumped to a surge tank, from which it is fed into the next process (concentration).

The residual slurry on the filter pans is washed in three stages by a continuous countercurrent stream to remove additional phosphoric acid. These streams ultimately recycle into the digestor system and the filter cake is washed from the filter by recycled contaminated water (gypsum pond water) and pumped to the gypsum pond for cooling and solids settling.

Wet process phosphoric acid production conditions are shown in Table 8.

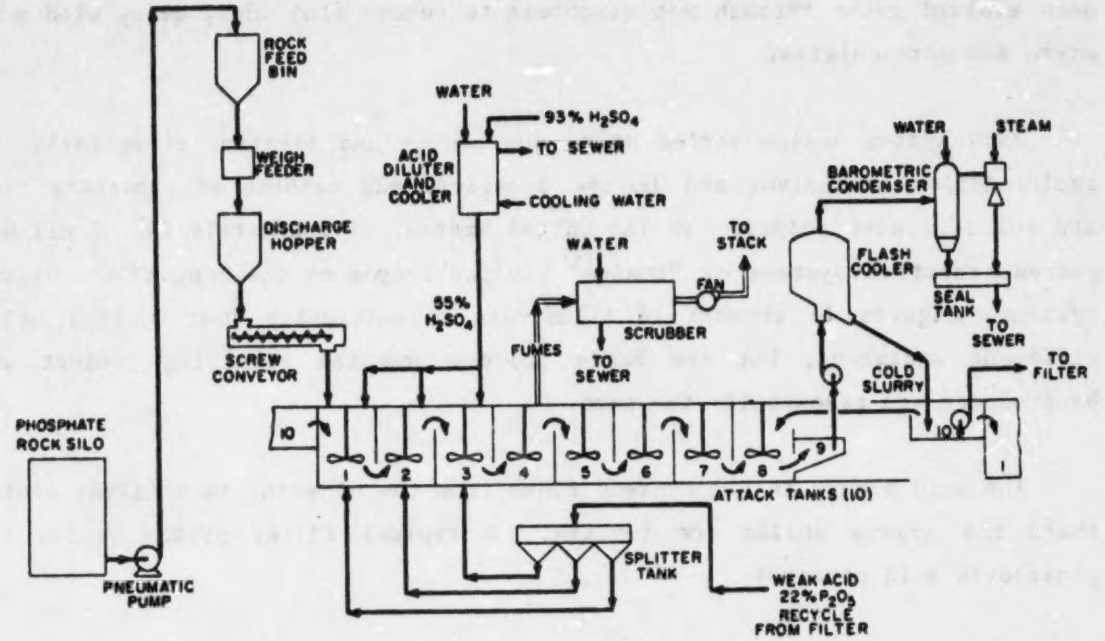
ROCK FEED BIN
WEIGH FEEDER
DISCHARGE HOPPER
SCREW CONVEYOR
PHOSPHATE ROCK SILO
PNEUMATIC PUMP
WATER
93% H_2SO_4
TO SEWER
ACID DILUTER AND COOLER
COOLING WATER
55% H_2SO_4
WATER
TO STACK
FAN
SCRUBBER
FUMES
TO SEWER
WATER
STEAM
BAROMETRIC CONDENSER
FLASH COOLER
SEAL TANK
TO SEWER
COLD SLURRY
TO FILTER
10
1
2
3
4
5
6
7
8
9
10
1
ATTACK TANKS (10)
SPLITTER TANK
WEAK ACID 22% P_2O_5 RECYCLE FROM FILTER

Figure 11. Flow diagram for Prayon phosphoric acid plant.

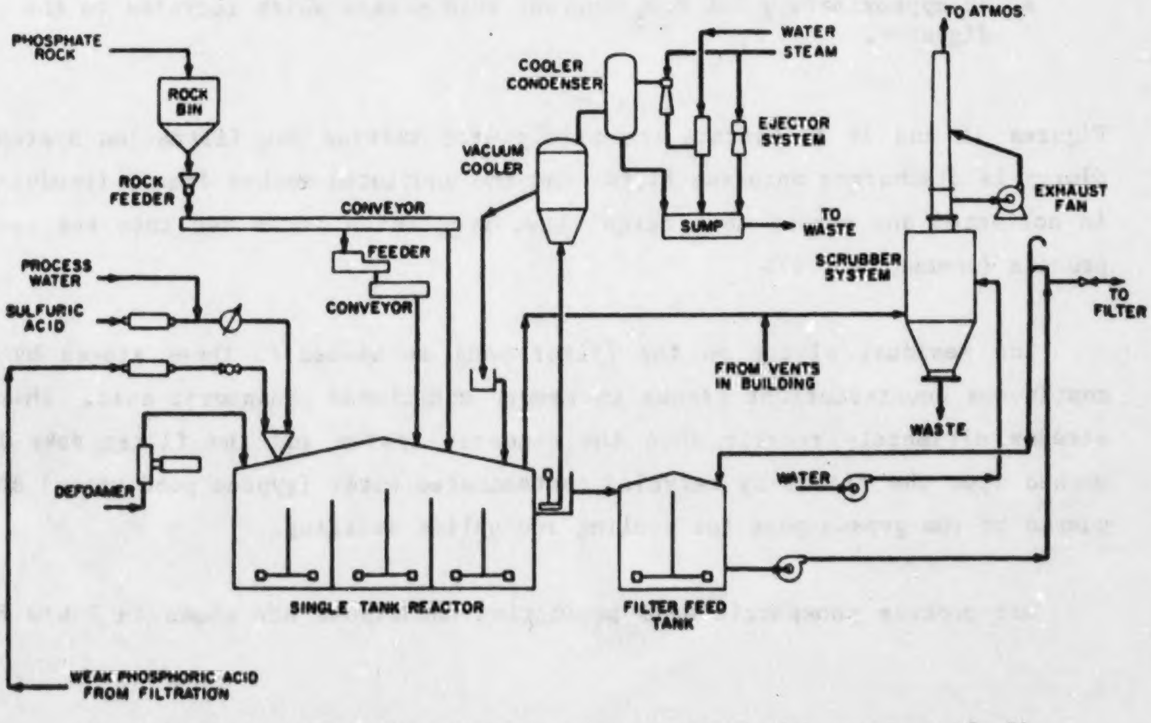
PHOSPHATE ROCK
ROCK BIN
ROCK FEEDER
CONVEYOR
FEEDER
CONVEYOR
PROCESS WATER
SULFURIC ACID
DEFOAMER
WEAK PHOSPHORIC ACID FROM FILTRATION
SINGLE TANK REACTOR
COOLER CONDENSER
VACUUM COOLER
WATER
STEAM
EJECTOR SYSTEM
SUMP
TO WASTE
TO ATMOS.
EXHAUST FAN
SCRUBBER SYSTEM
TO FILTER
FROM VENTS IN BUILDING
WASTE
WATER
FILTER FEED TANK

Figure 12. Dorr-Oliver reaction system (vacuum-cooled).

Figures 11 and 12 reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc., Year of first publication 1968.

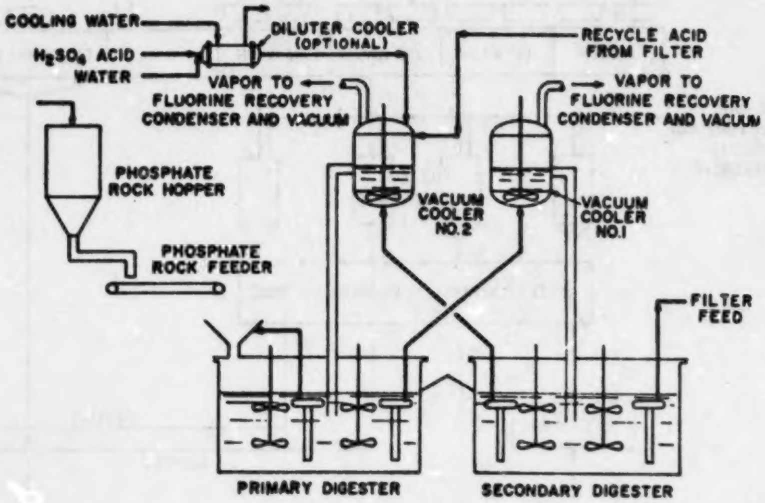
COOLING WATER
H_2SO_4 ACID
WATER
DILUTER COOLER (OPTIONAL)
RECYCLE ACID FROM FILTER
VAPOR TO FLUORINE RECOVERY CONDENSER AND VACUUM
VAPOR TO FLUORINE RECOVERY CONDENSER AND VACUUM
PHOSPHATE ROCK HOPPER
PHOSPHATE ROCK FEEDER
VACUUM COOLER NO.2
VACUUM COOLER NO.1
FILTER FEED
PRIMARY DIGESTER
SECONDARY DIGESTER

Figure 13. Flow diagram for Singmaster and Breyer dihydrate phosphoric acid process.

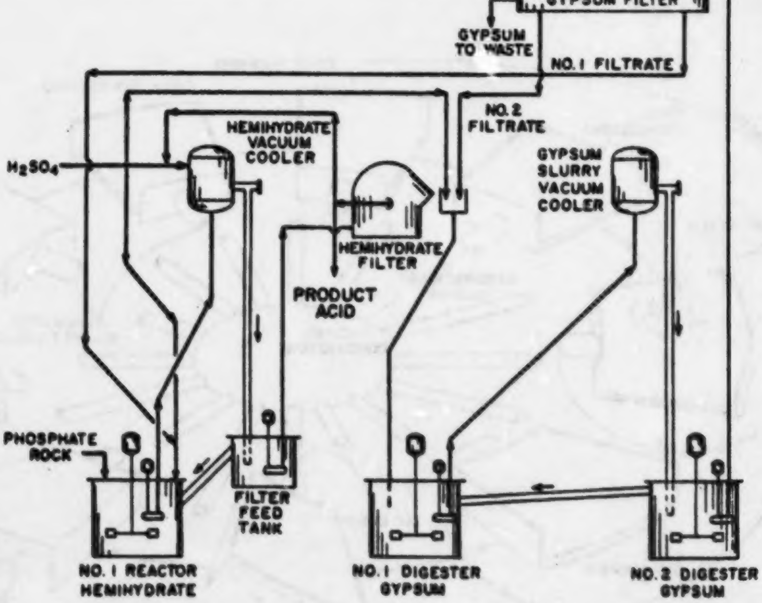
WATER
GYPSUM FILTER
GYPSUM TO WASTE
NO.1 FILTRATE
NO.2 FILTRATE
HEMIHYDRATE VACUUM COOLER
H_2SO_4
GYPSUM SLURRY VACUUM COOLER
HEMIHYDRATE FILTER
PRODUCT ACID
PHOSPHATE ROCK
FILTER FEED TANK
NO.1 REACTOR HEMIHYDRATE
NO.1 DIGESTER GYPSUM
NO.2 DIGESTER GYPSUM

Figure 14. Flow diagram of Singmaster and Breyer hemihydrate-dihydrate process.

Figures 13 and 14 reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc., Year of first publication 1968.

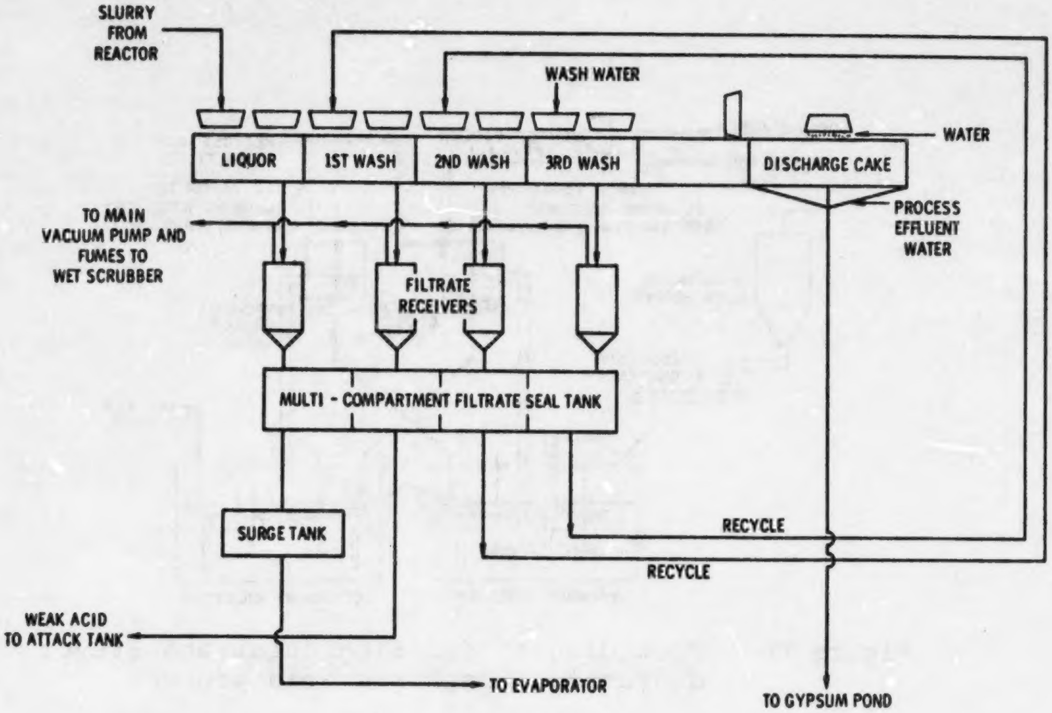
SLURRY FROM REACTOR
WASH WATER
WATER
LIQUOR
1ST WASH
2ND WASH
3RD WASH
DISCHARGE CAKE
TO MAIN VACUUM PUMP AND FUMES TO WET SCRUBBER
PROCESS EFFLUENT WATER
FILTRATE RECEIVERS
MULTI - COMPARTMENT FILTRATE SEAL TANK
SURGE TANK
RECYCLE
RECYCLE
WEAK ACID TO ATTACK TANK
TO EVAPORATOR
TO GYPSUM POND

Figure 15. Tilting pan filtration system.

Source: U.S. Department of Health, Education, and Welfare. 1970. Atmospheric emissions from wet process phosphoric acid manufacture. Raleigh NC, 86 p. in USEPA 1979a.

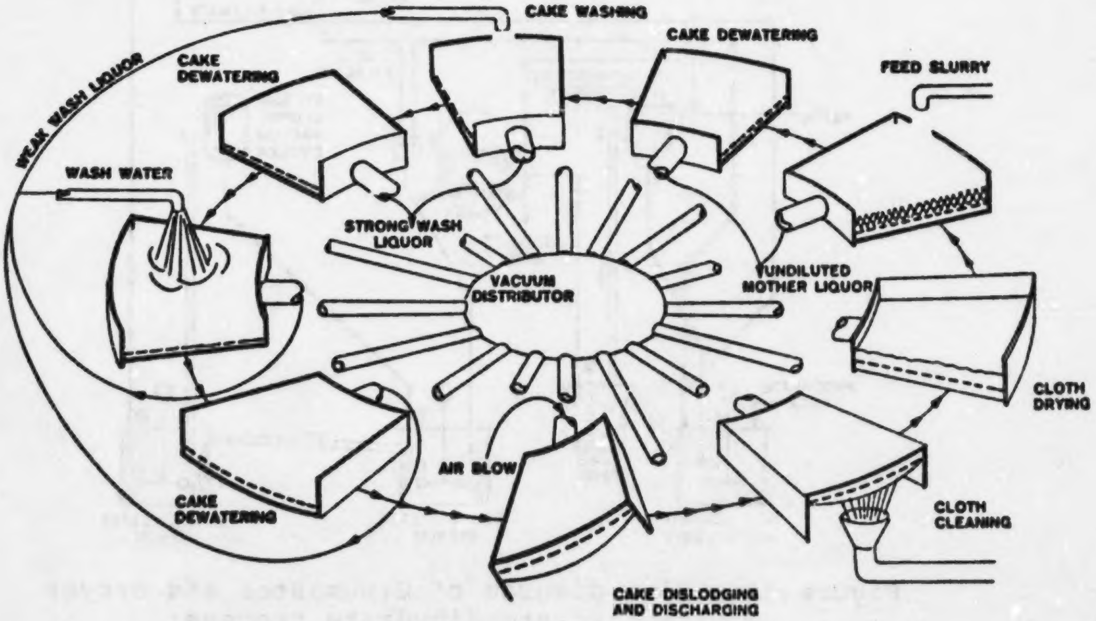
CAKE WASHING
CAKE DEWATERING
FEED SLURRY
WEAK WASH LIQUOR
CAKE DEWATERING
WASH WATER
STRONG WASH LIQUOR
VACUUM DISTRIBUTOR
UNDILUTED MOTHER LIQUOR
CLOTH DRYING
AIR BLOW
CAKE DEWATERING
CLOTH CLEANING
CAKE DISLODGING AND DISCHARGING

Figure 16. Operating cycle of rotary horizontal tilting pan filter.

Reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc., Year of first publication 1968.

Table 8. Wet process phosphoric acid production.

Input Materials

- Phosphate rock (ground)
- Sulfuric acid

Utilities

- Steam (from sulfuric acid process)
  - for vacuum induction when vacuum flash coolers are used
  - in stream ejectors to clean noncondesibles in systems using flash coolers
- Cooling water
- Process water
- Electrical energy

Waste Streams

- Tail gas
  - particulates of phosphate rock
  - sulfur oxides and acid mists
  - fluorides
- Gypsum solids
- Contaminated water (from cooling and scrubbers)

Product

- Phosphoric acid (26-32% P_2O_5)
  - this is an intermediate product
  - product is too weak for either sale or for econimic use in other phosphate fertilizer products
  - product is passed to next process for concentration

Note: Fluorides and, to a minor extent, gypsum can also be treated as recoverable coproducts. These products of pollution control systems are discussed in Section 3.0.

1.3.2.5 Phosphoric Acid Concentration

The phosphoric acid produced in the sulfuric acid digestion process is too low in concentration for sale or for processing of dry phosphate fertilizers. Concentration of the 26-32% P_2O_5 phosphoric acid is accomplished by vacuum evaporation of water from the acid solution. The acid is circulated through a shell-and-tube heat exchanger and then through a series of three flash chambers under vacuum pressure conditions, each separated by a shell-and-tube heat exchanger, as shown in Figure 17. The flash chambers or evaporators provide comparatively large liquid surface areas where water vapor can be released with minimum phosphoric acid entrainment.

Some of the phosphoric acid along with minor acid impurities, including fluorides, volatilize with the water vapor. The evolved vapors pass to a barometric condenser, where they are condensed and, along with condensed steam and process cooling water, flow to a hot well. From the hot well the contaminated water is recycled back to the phosphoric acid reaction process, where it is fed into the barometric condenser used with the acid flash cooler. Vapors from the hot well are vented to the wet scrubber system.

The above process describes a tube-type forced-circulation evaporator. It is the prevailing method currently in use, largely because it tends to generate fewer air emissions than other methods. This is so because practically all the vapors are condensed (Slack 1968). Operating conditions, however, are harsh. The acid stream is very corrosive and special non metallic materials must be used for construction. Precipitation of solids within the system is also a chronic problem that has been partically solved but still prompts continuous research and development of equipment and process modifications. Efficiency of the process depends on composition of the feed and its level of impurities, and on available utilities, such as cooling water and steam sources; but a properly designed forced-circulation evaporator can recover over 99.5% of the P_2O_5 during concentration of acid from 30 to 54%.

Industry and process design engineers (Slack 1968) have noted that phosphoric acid concentration and clarification in most operations are now considered part of the phosphoric acid process. The utility streams are integrated between and among the process units in most installations. Waste streams are generally treated by the same equipment. Common scrubbers are used for the emissions, and wastewater contaminants are incorporated into the common contaminated water system.

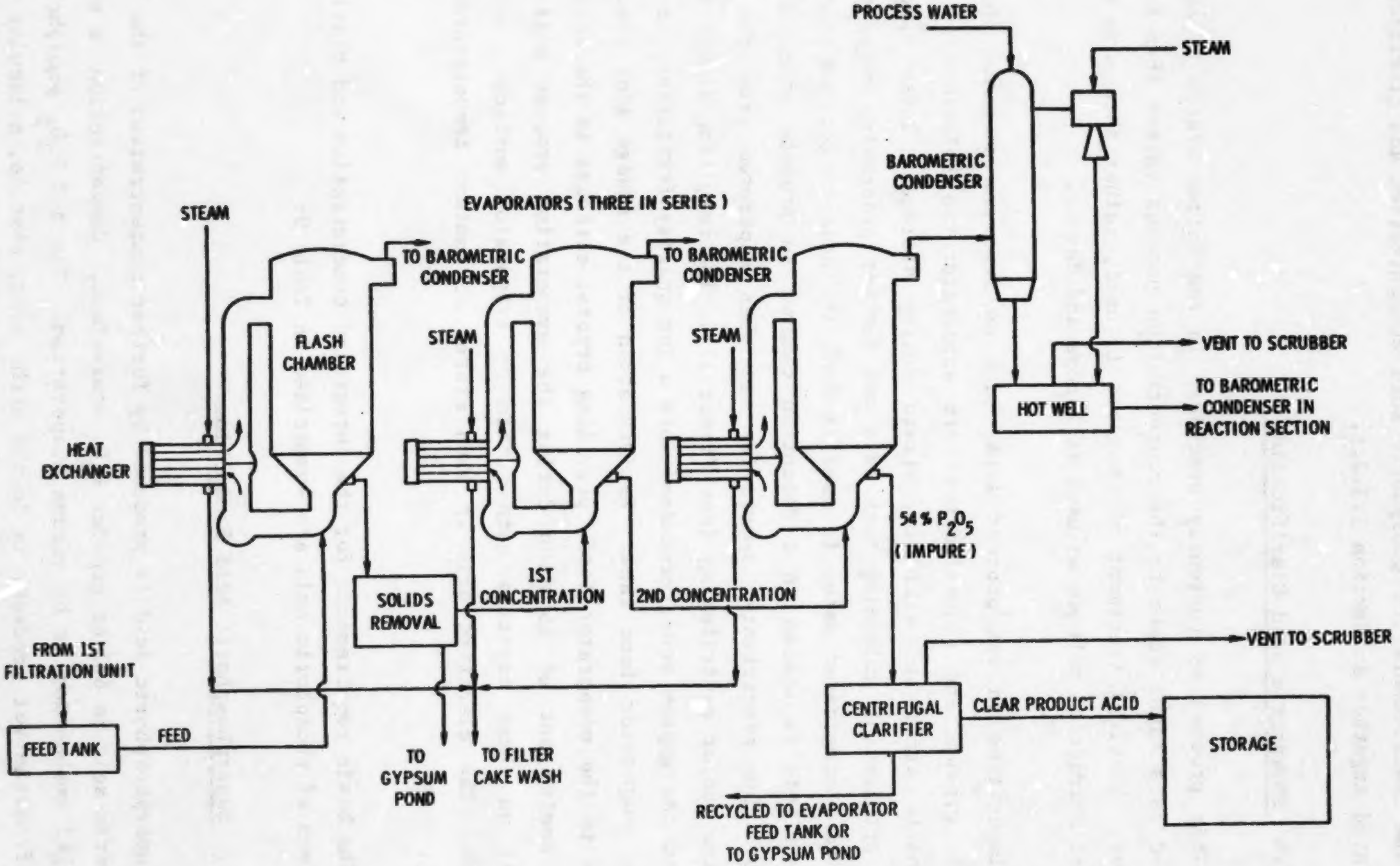
PROCESS WATER
STEAM
BAROMETRIC CONDENSER
EVAPORATORS (THREE IN SERIES)
STEAM
TO BAROMETRIC CONDENSER
TO BAROMETRIC CONDENSER
FLASH CHAMBER
STEAM
STEAM
VENT TO SCRUBBER
TO BAROMETRIC CONDENSER IN REACTION SECTION
HOT WELL
HEAT EXCHANGER
54% P2O5 (IMPURE)
SOLIDS REMOVAL
1ST CONCENTRATION
2ND CONCENTRATION
FROM 1ST FILTRATION UNIT
VENT TO SCRUBBER
CENTRIFUGAL CLARIFIER
CLEAR PRODUCT ACID
STORAGE
FEED TANK
FEED
TO GYPSUM POND
TO FILTER CAKE WASH
RECYCLED TO EVAPORATOR FEED TANK OR TO GYPSUM POND

Figure 17. Concentration and clarification of phosphoric acid.

Source: U.S. Department of Health, Education and Welfare. 1970. Atmospheric emissions from wet-process phosphoric acid manufacture. Raleigh NC, 86 p. in USEPA 1979a.

The requirements for phosphoric acid concentration and clarification are tabulated together in Section 1.3.2.6.

1.3.2.6 Phosphoric Acid Clarification

This process as currently practiced in the United States is often considered as a final stage to the concentration process rather than full scale process. Physical treatment of the acid is used, rather than more expensive solvent extraction methods as used in Europe and Mexico.

Impurities in wet process acid, such as iron and aluminum phosphates, soluble gypsum, and fluosilicates form supersaturated solutions in 54% P_2O_5 phosphoric acid, and will precipitate during storage. These precipitates cause problems in unloading tank cars and further processing using the acid. Recycled contaminated water is used to cool the acid to optimum temperatures and the acid is stored in a detention chamber to promote precipitation of solids. The precipitated impurities are then separated from the acid by settling and/or centrifuging (see Figure 17). The resulting sludge is either sent to the gypsum pond, processed into a low quality fertilizer, or recycled to the evaporator feed tank. Recirculation of the sludge adds precipitated solids to the evaporator feed, providing crystal surfaces in the acid. Since salts coming out of solution during the evaporation process will tend to deposit on these crystals rather than on evaporator surfaces, scaling is reduced. The clarified acid is then stored at ambient temperatures (USEPA 1979a).

The basic requirements for the integrated concentration and clarification processes of phosphoric acid are summarized in Table 9:

1.3.2.7 Superphosphoric Acid Production

Superphosphoric acid is produced by further concentration of the 54% P_2O_5 phosphoric acid to 66% or greater P_2O_5 equivalent. Concentration is either by submerged combustion or by vacuum evaporation. The 54% P_2O_5 phosphoric acid feed, from the wet process, is in the ortho form; that is, molecular composition is H_3PO_4. In the concentration process, elevated temperatures cause molecular dehydration and molecules combine into polyphosphoric acid chains

Table 9. Concentration and clarification of wet process phosphoric acid.

Input Materials

- Phosphoric acid (26-32% P_2O_5)

Utilities

- Steam (for vacuum condensers, heat exchangers, and flushing barometric condensers)
- Process water (for barometric condensers and acid cooling)
- Electrical energy (blowers, pumps, and scrubbers)

Waste Streams

- Contaminated water (from cooling and condensers)
- Emissions (fluorides and acid mist from hot well)
- Acid sludge

Product

- Concentrated phosphoric acid (54% P_2O_5), used for
  - salable product
  - production of triple superphosphate
  - production of ammonia phosphates
  - further concentration to superphosphoric acid
  - production of dry mixed and liquid blend fertilizers
- Acid sludge (potential coproduct for sale as low analysis fertilizer if not handled as a solid waste)

(USEPA 1979a). For example, tripolyphosphoric acid is formed by the following reaction:

$$3H_3PO_4 \rightarrow H_5P_3O_{10} + 2H_2O$$

Superphosphoric acid (SPA) is a mixture of orthophosphoric acid and polyphosphoric acid molecules of differing chain lengths. Wet process acid is normally concentrated to 68.5 to 72% P_2O_5 by conventional processes.

Major impurities in wet process phosphoric acid are calcium, iron, aluminum, magnesium, potassium, sodium, fluorine (HF, H_2SiF_6, SiF_4), and sulfate. These materials precipitate at different temperatures and acid concentrations, but one overall effect is great potential for scaling and high viscosity. The concentration processes used commercially are designed to restrict scaling and clogging problems.

Submerged Combustion

This process takes advantage of an old maxim that "no scale can grow on a bubble" and effects heat transfer primarily by bubbling a stream of hot combustion gas through the phosphoric acid solution (Slack 1968). A study by USEPA (USEPA 1974b) noted that this process is considered outmoded and unlikely to be used in the future. In addition, gaseous emissions are highly polluting and difficult to control. Currently, only two United States plants (accounting for approximately 26% of SPA production) use submerged combustion (USEPA 1979a). The fact that submerged combustion also entails high energy consumption in the form of natural gas, make it an unlikely option for new source facilties.

Vacuum Evaporation

Seven plants in the United States (Section 1.5.1) produce SPA by vacuum evaporation; four use the Stauffer falling film evaporator and three use the Swenson forced circulation evaporator. The Stauffer process and the Swenson process are shown in Figures 18 and 19. The basic processes have been described by Rawlings, et al. (USEPA 1979a):

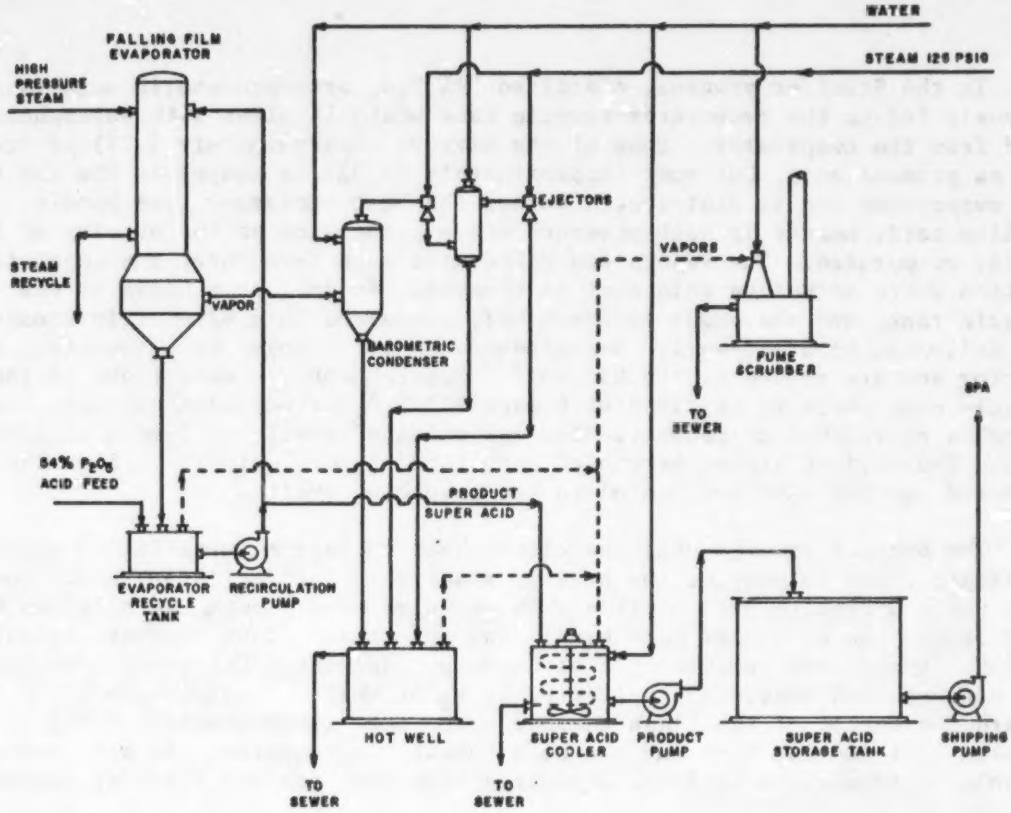
WATER
STEAM 125 PSIG
FALLING FILM EVAPORATOR
HIGH PRESSURE STEAM
EJECTORS
VAPORS
STEAM RECYCLE
VAPOR
BAROMETRIC CONDENSER
FUME SCRUBBER
SPA
TO SEWER
54% P_2O_5 ACID FEED
PRODUCT SUPER ACID
EVAPORATOR RECYCLE TANK
RECIRCULATION PUMP
HOT WELL
SUPER ACID COOLER
PRODUCT PUMP
SUPER ACID STORAGE TANK
SHIPPING PUMP
TO SEWER
TO SEWER

Figure 18. Stauffer process for wet process superphosphoric acid.

Source: Barber, J.C. 1979. Falling film evaporator process. Adapted from TVA file drawings. Florence AL.

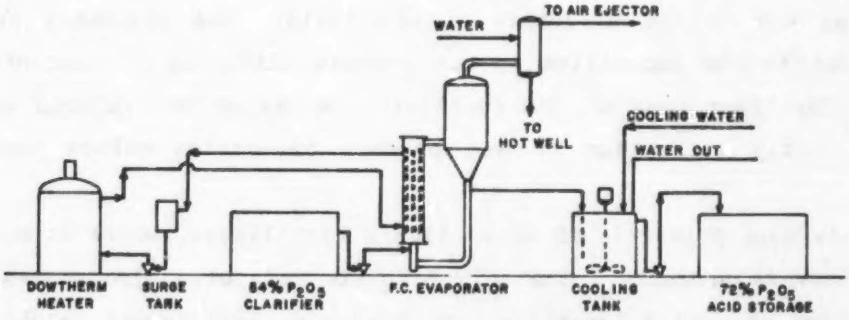
TO AIR EJECTOR
WATER
TO HOT WELL
COOLING WATER
WATER OUT
DOWTHERM HEATER
SURGE TANK
54% P_2O_5 CLARIFIER
F.C. EVAPORATOR
COOLING TANK
72% P_2O_5 ACID STORAGE

Figure 19. Vacuum evaporation SPA concentration processes.

Source: Adapted from Rushton, W.E. 1966. Swenson superphosphoric acid process. Phosphorus and Potassium No. 23, June/July, p. 13-16, 19.

In the Stauffer process, clarified 54% P_2O_5 orthophosphoric acid is continously fed to the evaporator recycle tank where it mixes with superphosphoric acid from the evaporator. Some of the mixture (approximately 1.2%) is drawn off as product acid, but most (approximately 98.8%) is pumped to the top of the evaporator and is distributed across the heat exchanger tube bundle. The falling acid, heated by high-pressure steam condensing on the outside of the tubes, evaporates. The vapors and dehydrated acid then enter the separator section where entrained acid mist is removed. Product acid flows to the recycle tank, and the vapor is drawn off, condensed in a barometric condenser, and delivered to a hot well. Noncondensables are removed by a two-stage steam ejector and are vented to the hot well. Superphosphoric acid flows to the recycle tank where it is mixed with more 54% P_2O_5 orthophosphoric acid, and recycled or removed as product. The approximate recycle to feed acid ratio is 80:1. The product stream is cooled and stored before shipping. Both the hot well and cooling tank are vented to wet scrubbing systems.

The Swenson process utilizes closed heat exchanger tubes filled with heat exchanger fluid to provide the heat of reaction. Feed acid (54% P_2O_5) pumped into the evaporating system mixes with recycled superphosphoric acid. As the acid leaves the exchanger tube bundle and enters the flash chamber, evaporation begins. Vapors are removed by a barometric condenser. Condensed materials and noncondensed vapors are delivered to a hot well. Product acid flows toward the bottom of the flash chamber where part (approximately 0.6%) is removed to a cooling tank and the rest (99.4%) is recycled. An approximate recycle to feed ratio is 150:1 (compared with 80:1 for the Stauffer process).

Cooling in both systems is accomplished by circulating water through stainless steel tubes in the holding tank.

72% P_2O_5 is the maximum concentration practical for commercial production (Dinauer 1971). Any higher concentrations of wet process acid cause handling problems including pump failure, valve and tubing breakdowns, and overheating of motors, due to the viscosity of the fluid. The viscosity problems are largely due to the impurities in wet process acid. Higher concentrations and many non fertlizer uses of SPA therefore require either furnace acid derivation or costly extraction of wet process impurities before concentration.

SPA is used primarily in mixed liquid fertilizers, where it makes possible higher analysis products. The polyphosphate molecules also sequester some of the iron and magnesium impurities which attain their lowest solubility around the 54% P_2O_5 concentration level for wet process acid, and would cause handling problems if in liquid fertilizers. Early anticipated marketing advantages of SPA in reducing shipping costs as compared with less concentrated phosphoric acid have not been realized due to its handling problems.

A summary inventory of the process requirements follows:

Table 10. Superphosphoric acid production.

Input Materials

- 54% P_2O_5 phosphoric acid

Utilities

- Steam (from sulfuric acid process or auxiliary steam boiler)
- Electrical energy (pumps, circulators, blowers)
- Cooling water
- Natural gas (submerged combustion process)

Waste Streams

- Fluoride emissions
- Sulfur oxides
- Acid mist
- Combustion products (submerged combustion process)

Products

- Superphosphoric acid (68.5 to 72% P_2O_5), used primarily for production of liquid mixed fertilizers
- Fluorine in the form of CaF_2 or fluosilicic acid are recovered as coproducts at some installations

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Note: SPA production is normally included under existing effluent guidelines for the phosphate fertilizer manufacturing subcategory. Since SPA is produced at such facilities and since it can utilize the common contaminated wastewater system, there is no contradiction implied in the fact that the process is not specifically identified in effluent guidelines. It was not intended that the process be excluded; it simply was not chosen to be addressed in the Development Document for basic fertilizer chemicals (USEPA 1974a); By telephone. Dr. Elwood Martin, USEPA, Effluent Guidelines Division, March 27, 1979).

1.3.2.8 Triple Superphosphate Production

Triple superphosphate (TSP) is a high analysis phosphate fertilizer (46 to 48.5% P_2O_5 content). TSP can be produced either as run of pile (ROP) or as granular triple superphosphate (GTSP). ROP and GTSP can be manufactured in batch or continuous process modes. ROP triple superphosphate can be used in hot-mixed fertilizers whereas GTSP is preferable for use in dry bulk blends or for direct application. ROP, however, involves difficult air pollution problems due to dust and can cause materials handling problems if shipment is involved. Most new plants are expected to produce the granular type TSP.

Both processes utilize the same raw materials, ground phosphate rock and approximately 54% P_2O_5 phosphoric acid. The basic chemical reaction takes place by the following reaction (USEPA 1974a):

$$Ca_3(PO_4)_2 + 4(H_3PO_4) + 3H_2O \rightarrow 3Ca(H_2PO_4)_2 \bullet H_2O$$

The overall reaction, taking into account the fate of fluorine in the fluorapatite ore is as follows (USEPA 1971):

$$3Ca_3(PO_4)_2 + CaF_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2 \bullet H_2O + 2HF$$

As is the case in normal superphosphate, the HF reacts with silica to form SiF_4, which partially hydrolyzes to form fluosilicic acid (H_2SiF_6) and is partially evolved as gas. As with NSP, SiF_4 and H_2SiF_6 are also evolved during denning, curing, and storage operations. The similarity between the ROP and GTSP processes, however, does not go beyond the initial acidulation operation.

Run of Pile TSP Production

The ROP process is virtually identical to the NSP process except that phosphoric acid is used instead of sulfuric acid. Figure 20 shows a flow diagram of the process. Batch mode is carried out in older plants, but continuous process mode is assumed for process discussion.

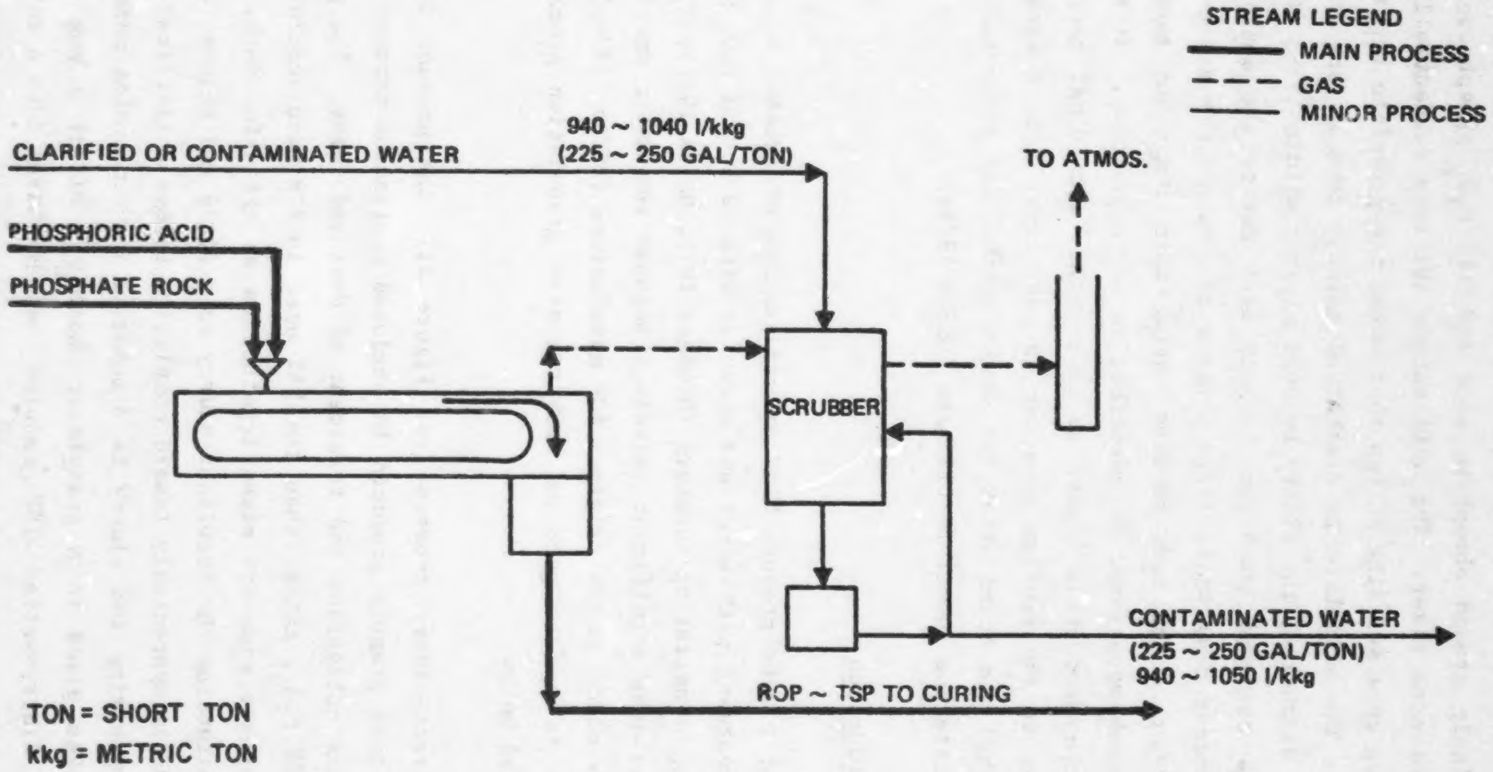
STREAM LEGEND
MAIN PROCESS
GAS
MINOR PROCESS
940 ~ 1040 l/kkg
(225 ~ 250 GAL/TON)
CLARIFIED OR CONTAMINATED WATER
TO ATMOS.
PHOSPHORIC ACID
PHOSPHATE ROCK
SCRUBBER
CONTAMINATED WATER
(225 ~ 250 GAL/TON)
940 ~ 1050 l/kkg
ROP ~ TSP TO CURING
TON = SHORT TON
kkg = METRIC TON

Figure 20. Triple superphosphate (run of pile) (flow rate per ton ROP).

Source: Adapted from U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC.

Most facilities use the continuous cone mixer process developed by TVA in the 1930's. Finely ground phosphate rock and 54% P_2O_5 phosphoric acid are metered into the cone mixer. The acid enters the cone tangentially at high velocity, setting up a swirling action that mixes the materials within seconds (Dinauer 1971). The acidulate is discharged quickly onto a long rubber conveyor belt. On discharge, the slurry becomes plastic within 15 to 30 seconds. The material is conveyed to a den (or, in many cases, the conveyor moves through a continuous den) where large amounts of noxious gas are evolved and vented to scrubbers. The mass hardens during this stage and takes on the vesicular honeycomb appearance as described in NSP production. At the end of the conveyor, the product is broken up in a rotary mechanical cutter before being discharged to the storage area for an additional 2 to 4 weeks curing. Product is crushed and sized after the curing period and processed for shipping or for on-site use in mix fertilizers (USEPA 1974a).

Granular TSP Production

A number of plants produce GTSP by utilization of crushed or ground ROP material and treatment with water and steam or with 38 to 40% P_2O_5 phosphoric acid in rotating or agitating chambers (Dinauer 1971, USEPA 1971). Those processes do not produce significant emissions because the major portion of the fluorides were evolved in the original ROP manufacture (USEPA 1974b), but the product quality is not as good as with one-step granulation process (USEPA 1977c), described below.

In the direct-slurry process (see Figure 21), the product is a hard, uniform, pellitized granule produced in enclosed continuous process equipment which facilitates collection and treatment of dust and fumes. The phosphoric acid used is 40% P_2O_5, rather than the 54% used in ROP manufacture. The acid and ground phosphate rock are mixed together in an agitating tank. The lower strength acid maintains the resultant slurry as a fluid and allows the chemical reaction to proceed appreciably toward completion before solidification starts. After 1-2 hours mixing the slurry is discharged onto recycled undersize dry GTSP. This takes place in a granulator chamber - either a pug mill or a rotating drum. Slurry-wetted GTSP granules then discharge into a rotary dryer where the chemical reaction is accelerated and excess water removed by the dryer heat. Dried granules are next sized on vibrating screens. Over- and

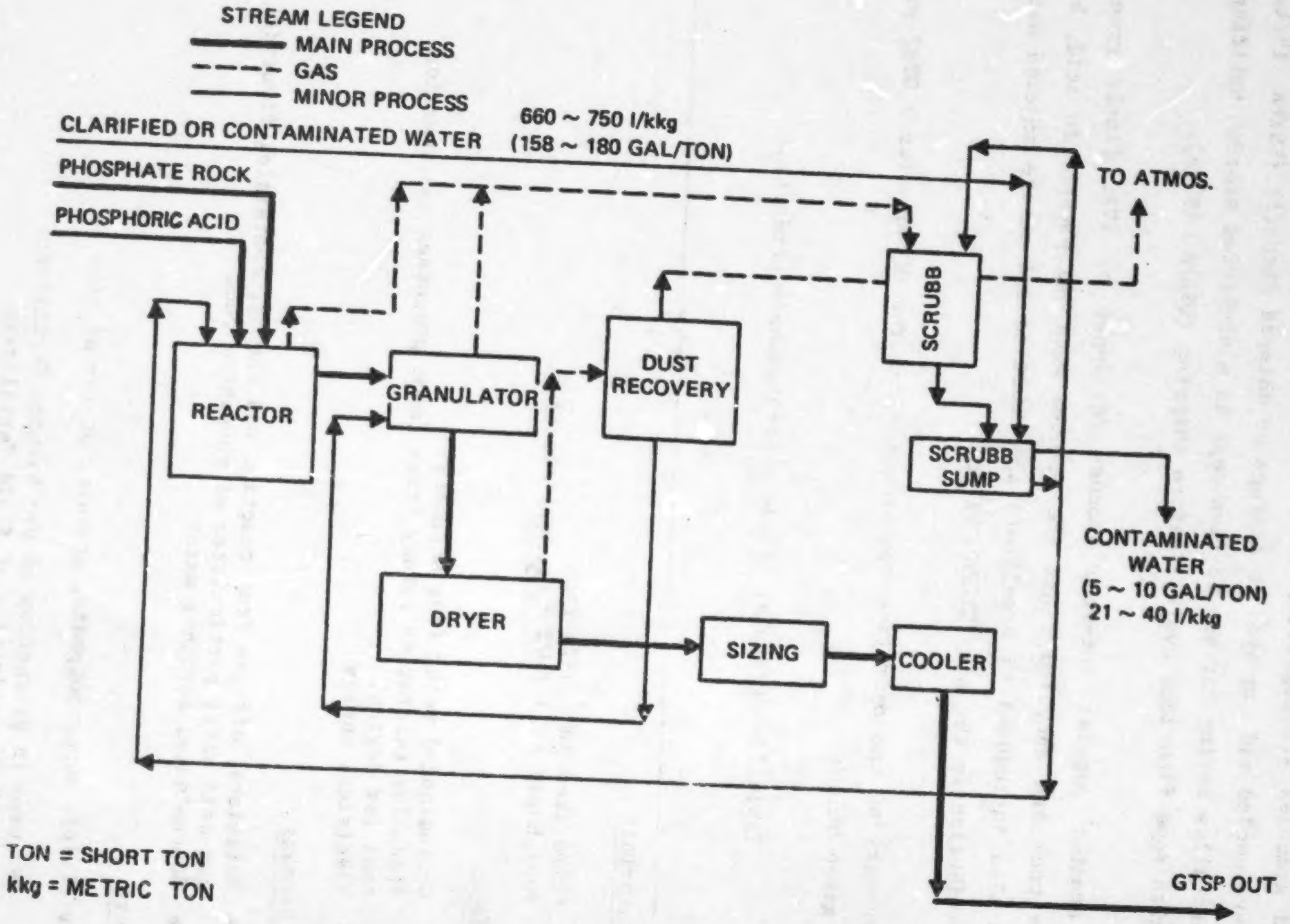
STREAM LEGEND
MAIN PROCESS
GAS
MINOR PROCESS
CLARIFIED OR CONTAMINATED WATER
660 ~ 750 l/kkg
(158 ~ 180 GAL/TON)
PHOSPHATE ROCK
PHOSPHORIC ACID
REACTOR
GRANULATOR
DUST RECOVERY
SCRUBB
SCRUBB SUMP
DRYER
SIZING
COOLER
TO ATMOS.
CONTAMINATED WATER
(5 ~ 10 GAL/TON)
21 ~ 40 l/kkg
GTSP OUT
TON = SHORT TON
kkg = METRIC TON

Figure 21. Granulated triple superphosphate (flow rate per ton GTSP).

Source: Adapted from U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC.

undersized granules are separated and used as recycle material. Product size granules are cooled and conveyed to storage or shipped directly (USEPA 1974a). Most plants allow curing for one to five days in a sheltered storage building, during which some fluorides evolve, before shipping (USEPA 1977c).

In another popular one-step process developed by TVA, finely ground phosphate rock and recycled fines are reacted with 54% phosphoric acid, but steam is also introduced to accelerate the reaction and ensure an even moisture distribution in the mix (USEPA 1977c).

A summary of the operating requirements for the direct-slurry GTSP process is given below:

Table 11. Granular triple superphosphate production.

Input Materials

- Pulverized phosphate rock
- Phosphoric acid (40% P_2O_5 equivalent)

Utilities

- Contaminated water (for scrubber)
- Steam for reactor or rotary drier (some processes use reaction heat for drying)
- Electrical energy

Waste Streams

- Emissions, off-gas from reaction and curing, containing fluorides and acid mist; particulates of phosphate rock
- Contaminated scrubber water

Products

- Triple superphosphate, granular or run of pile
    - used in production of dry blended fertilizers
    - used in production of fluid fertilizers
- Fluorine, in the form of CaF_2 or fluosilicic acid, are recovered as coproducts by some manufacturers

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1.3.2.9 Ammonium Phosphate Production

Monoammonium phosphate (MAP) and diammonium phosphate (DAP) are basic concentrated fertilizer materials containing N and P, used in bulk blend fertilizers and to some extent for direct application. Ammonium polyphosphates, conventionally produced by reacting SPA with ammonia, are considered to be mixed fertilizers and currently are used primarily in fluid fertilizers. Although not included in the phosphate subcategory, APP processes and products commonly include MAP and DAP production. For this reason a discussion of APP's is included in this section.

Monoammonium Phosphate and Diammonium Phosphate Production

Ammonium phosphate fertilizers include a variety of formulations which differ in the amounts of nitrogen and phosphorus present. In the United States the most important grades are:

MAP: 11-48-0
13-52-0
11-55-0*
16-20-0
DAP: 16-48-0**
18-46-0

*15 to 25% P_2O_5 equivalent is APP (L.B. Nelson 1978 in TVA 1978a)
**approximately 1/3 MAP and 2/3 DAP (Dinauer 1971)

In a typical ammonium phosphate process 40% P_2O_5 phosphoric acid is partially reacted wtih ammonia in a preneutralizer or reactor (see Figures 22 and 23). The resultant slurry is sprayed or dripped onto a bed of fine recycled solids in an ammoniator-granulator. Additional ammonia is injected under the bed to complete reaction and resulting granules are dried and screened, with undersize material recycled to the ammoniator (Slack 1968a).

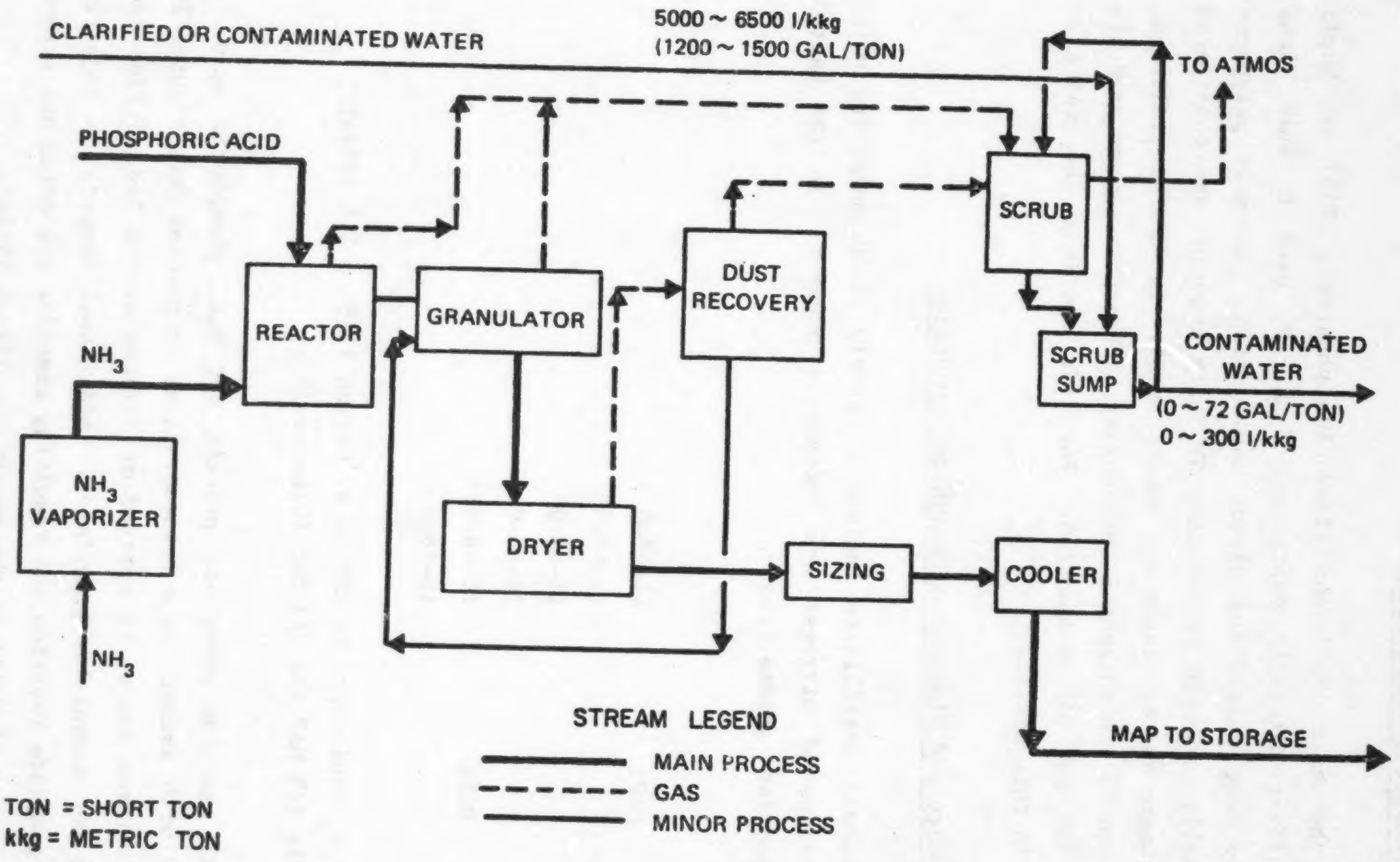

CLARIFIED OR CONTAMINATED WATER
5000 ~ 6500 l/kkg
(1200 ~ 1500 GAL/TON)
TO ATMOS
PHOSPHORIC ACID
SCRUB
DUST RECOVERY
REACTOR
GRANULATOR
SCRUB SUMP
CONTAMINATED WATER
(0 ~ 72 GAL/TON)
0 ~ 300 l/kkg
NH_3
NH_3 VAPORIZER
DRYER
SIZING
COOLER
NH_3
STREAM LEGEND
MAIN PROCESS
GAS
MINOR PROCESS
MAP TO STORAGE
TON = SHORT TON
kkg = METRIC TON

Figure 22. Monoammonium phosphate plant (flow rate per ton MAP).

Source: Adapted from U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC.

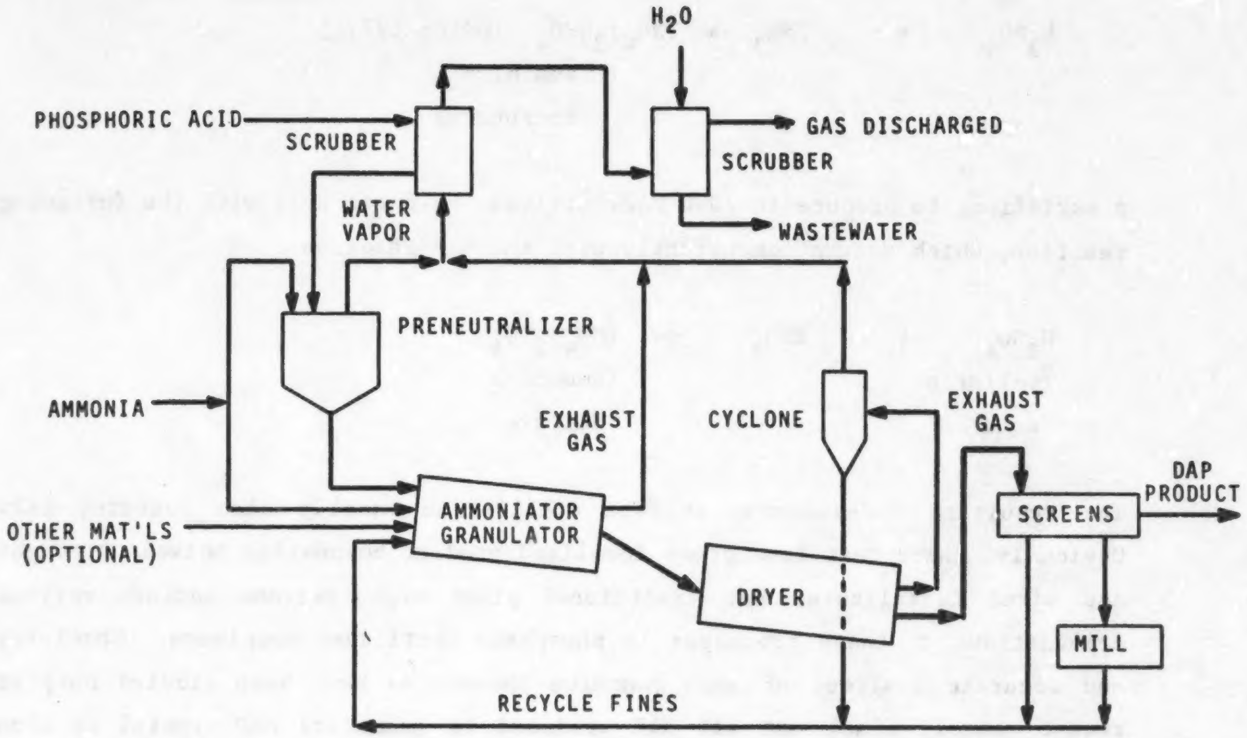

H_2O
PHOSPHORIC ACID
SCRUBBER
GAS DISCHARGED
SCRUBBER
WATER VAPOR
WASTEWATER
PRENEUTRALIZER
AMMONIA
EXHAUST GAS
CYCLONE
EXHAUST GAS
DAP PRODUCT
AMMONIATOR GRANULATOR
OTHER MAT'LS (OPTIONAL)
SCREENS
DRYER
MILL
RECYCLE FINES

Figure 23. Flowsheet for production of diammonium phosphate (DAP).

Source: U.S Environmental Protection Agency. 1971. Inorganic fertilizer and phosphate mining industries, Water pollution and control. Prepared by Battelle Memorial Institute. Richland WA, 226 p.

Basic reactions are as follows:

$$\underset{\text{(Phosphoric acid)}}{H_3PO_4} + \underset{\text{(Ammonia)}}{NH_3} \rightarrow \underset{\text{(Monoammonium Phosphate)}}{NH_4H_2PO_4} \quad \text{(USEPA 1974a) or,}$$

$$H_3PO_4 + 2NH_3 \rightarrow \underset{\text{(Diammonium Phosphate)}}{(NH_4)_2HPO_4} \quad \text{(USEPA 1977c)}$$

A variation, to produce 16-20-0 MAP, utilizes sulfuric acid with the following reaction, which occurs concurrently with the MAP reaction:

$$\underset{\text{(sulfuric acid)}}{H_2SO_4} + 2NH_3 \rightarrow \underset{\text{(Ammonium Sulfate)}}{(NH_4)_2SO_4}$$

The resulting MAP-ammonium sulfate combination usually also contains DAP. Obviously, these reactions cross idealized product boundaries between straight and mixed fertilizers, but traditional plant organizations include various combinations of these processes in phosphate fertilizer complexes. Chemistry and accurate analyses of some ammonium phosphates have been studied only in recent years. Also, not all MAP produced is granular; MAP crystal is also produced and crushed for use in granulation processes for mixed fertilizers. In MAP production only one preneutralizer tank is used, as opposed to two tanks which are used for DAP production.

Variations in ammonium phosphate production include use of nitric instead of sulfuric acid, which in combination with phosphoric acid produces nitric phosphate or ammonium phosphate nitrate. Another process arrangement allows the neutralization reaction to go to completion in a series of tanks before the product slurry is fed to a "blunger," which is a paddle mixer where granulation is completed with the addition of dried recycled fines, (Dinauer 1971), (USEPA 1977b). Another variation injects phosphoric acid directly onto a bed of recycled product fines in a rotary drum granulator and injects ammonia under the bed of fines. In this arrangement, neutralization and granulation occur in the same piece of equipment. Heat of ammoniation evaporates water in all these arrangements. (USEPA 1977b). In general, the end products are varied by the acids used and the N content is varied by the degree of ammoniation (Dinauer 1971).

Cyclone collectors and/or venturi scrubbers are used for dust and off-gas recovery and recycle in most systems. Wet scrubbers are used for end-of-process emissions control, using contaminated water. A summary of process requirements is presented below for ammonium phosphates production including MAP, DAP, and ammonium sulfates and nitrates:

Table 12. Ammonium phosphate production.

Input Materials

- Anhydrous ammonia
- Phosphoric acid (30-52% P_2O_5, depending on product)
- Sulfuric acid
- Nitric acid

Utilities

- Electrical energy for pumps, mills, fans, and blowers
- Fuel for drying - older processes (most recent processes use heat of ammoniation for drying)

Waste Streams

- Contaminated wastewater for scrubbers (or incoming phosphoric acid can be used)
- Air emissions - off-gases
  - ammonia
  - fluorides
  - phosphate rock particulates
  - acid-ammonia mists

Products

- Monoammonium phosphate
- Diammonium phosphate
- Ammonium phosphate nitrate and ammonium nitrate
- Ammonium sulfate
- Fluorides as CaF_2 or fluosilicic acid are potential coproducts

Process Variations

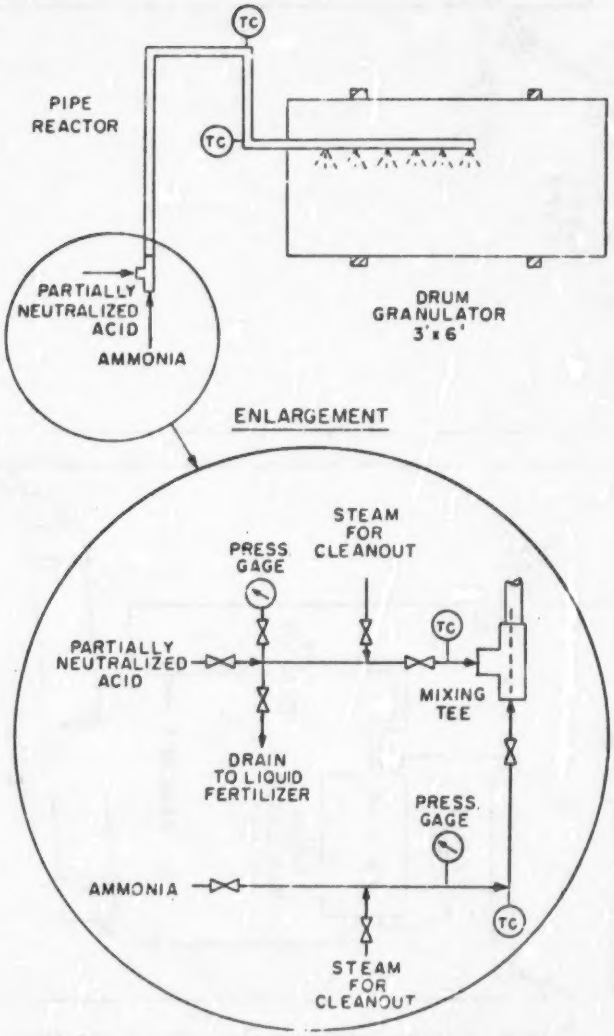
The basic MAP and DAP processes described above are in use in plants in the United States, but recent innovations in technology are being implemented at numerous locations, sometimes alongside an existing conventional process train, sometimes in new installations. In other cases, adaptations are made to existing conventional equipment to incorporate recent technology.

A wide range of process variations are in use. Many of these are proprietary, patented, or protected by company secrecy classification. Consequently, details are not readily available. Furthermore, manufacturers routinely innovate and operate using temporary process modifications for trial periods of several days to several months. If successful these modifications may be permanently installled. For these reasons, several basic process modifications are discussed below which are indicative of processes in use, although operational details vary from plant to plant. Reference is made to TVA processes described in pilot plant operations. Due to the cooperative relationship, however, between manufacturers and TVA, these processes are considered indicative of commercial operations.

Pipe Reactor

One of the most significant process developments for ammoniated granular fertilizers is the TVA pipe reactor, developed in 1971 (Nelson in TVA 1978a). The pipe reactor is a process modification in which the acid and ammonia are reacted in the delivery system and introduced under pressure into the granulation chamber (a pug mill or a drum type granulator) as an atomized melt. Figure 24 is a detail of a standard pipe reactor arrangement.

Figure 25 shows a pipe reactor system set up for a number of NPK formulations. NP products are produced by excluding the potassium chloride and urea feeds. A preneutralizer is used to blend part of the ammonia with the acid (NH_3:H_3PO_4 mole ratio of 0.4). This is done to prevent rapid scale formation downstream in the pipe reactor. In TVA demonstrations, and in some industry applications, the phosphoric acid feed to the preneutralizer is introduced at a metered rate to the scrubber handling the ammoniator-granulator exhaust



TC
PIPE REACTOR
TC
PARTIALLY NEUTRALIZED ACID
AMMONIA
DRUM GRANULATOR 3'x6'
ENLARGEMENT
STEAM FOR CLEANOUT
PRESS GAGE
TC
PARTIALLY NEUTRALIZED ACID
MIXING TEE
DRAIN TO LIQUID FERTILIZER
PRESS. GAGE
AMMONIA
TC
STEAM FOR CLEANOUT

Figure 24. Details of pipe reactor in drum granulator.

Source: Tennessee Valley Authority. 1974. New developments in fertilizer technology, 10th demonstration, October 1-2, 1974. National Fertilizer Development Center. Muscle Shoals AL, 72 p.

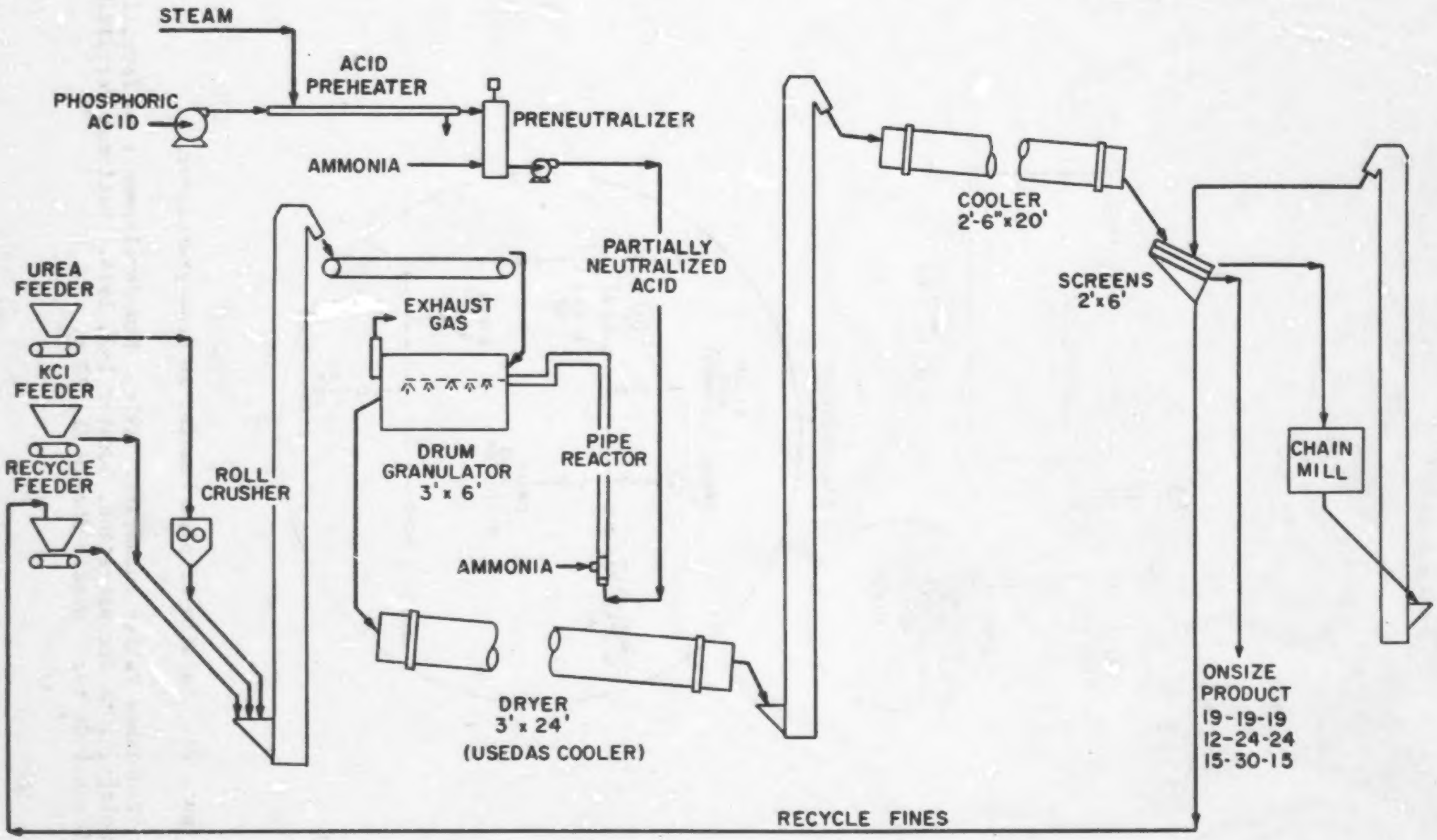

STEAM
PHOSPHORIC ACID
ACID PREHEATER
PRENEUTRALIZER
AMMONIA
PARTIALLY NEUTRALIZED ACID
UREA FEEDER
KCl FEEDER
RECYCLE FEEDER
ROLL CRUSHER
EXHAUST GAS
DRUM GRANULATOR 3' x 6'
PIPE REACTOR
AMMONIA
DRYER 3' x 24'
(USEDAS COOLER)
COOLER 2'-6" x 20'
SCREENS 2' x 6'
CHAIN MILL
ONSIZE PRODUCT
19-19-19
12-24-24
15-30-15
RECYCLE FINES

Figure 25. Flow diagram of granulation pilot plant using pipe reactor process for NPK fertilizers.

Source: Tennessee Valley Authority. 1974. New developments in fertilizer technology, 10th demonstration, October 1-2, 1974. National Fertilizer Development Center. Muscle Shoals AL, 72 p.

gases. Phosphoric acid is more effective than water for ammonia scrubbing and this arrangement also precludes introducing unwanted water into the process while recycling costly ammonia. The partially neutralized acid is blended with additional ammonia to achieve an $NH_3:H_3PO_4$ mole ratio of about 1.05 (Hicks 1977). This produces a melt (instead of the slurry in conventional processes) which is nearly anhydrous. Melt temperature is usually about 430 to 440 F (206-212 C) (TVA 1974). The melt is sprayed from the pipe reactor onto recycled fines, which they readily agglomerate. The drying takes place in a cooling chamber utilizing the heat of the melt to complete drying and solidification (conventional processes require natural gas heaters).

The TVA pipe reactor has largely replaced the tank reactor process (Nelson in TVA 1978a) and is currently among the more attractive systems available because emission problems are largely eliminated at the source. The method of mixing and reaction retards evolution of particulates and produce strong granules which generate fewer immediate dust problems and retard dust emissions in later handling also. The potential energy savings due to elimination of the need for a fuel-fired dryer has been a major factor in the interest in pipe reactor systems.

The pipe reactor process is undergoing continuous development by TVA and improvements have been made both by TVA and by the industry. A discussion of these modifications and their advantages follows. The first major improvement had to do with the preneutralizer tanks.

Conventional processes generally all use preneutralizer tanks, as does the original TVA pipe cross reactor process. For more than 17 years MAP and DAP processes have employed them. These tanks are usually constructed of stainless steel or of mild steel with a lining of acid brick. A plant may have either a single preneutralizer tank or several tanks in series, but in either case, the moisture content of the slurry can be pumped with a conventional centrifugal pump and uniformly distributed in a granulator. Because of this high moisture content, the granulator product must be dried. The following operating problems have been reported by companies that produce MAP and DAP in processes using preneutralizer tanks:

1. Difficulty in pumping and metering the hot slurry from the preneutralizer.
2. Foaming and boiling over of the slurry in the preneutralizer.
3. Difficulty in controlling the slurry level in the preneutralizer.
4. Plugging of the ammonia sparger and poor ammonia distribution in the preneutralizer.
5. Scarcity and high price of fuel needed for drying the product. (Parker et al. 1977).

The original pipe reactor put into operation by TVA in December 1973 did use the preneutralizer but the heat generated in the reaction tube was effective in evaporating much of the water and produced a slurry or melt much lower in moisture than those in conventional preneutralizer processes. This process, which also employed a pugmill, is shown in Figure 26. The nearly anhydrous melt produced contains 15 to 30% polyphosphate. Also, in this process the pipe-reactor melt enters a vapor disengager (see Figure 27) where helical rotary blades spread the melt to facilitate removal of water vapor (steam) and free ammonia and thus compact and defoam the melt. The melt flows by gravity down a short heated chute from the disengager to a double-shaft pugmill.

Recycle is fed to the pugmill, and composite scrubbing liquor from the dust-recovery system (about 40-50% concentration) is added after being heated in a steam-jacketed vessel containing internal steam coils. Fertilizer mixing plants have adopted this process for use in mixed formulations. An 11-55-0 grade APP can be produced using this process and the addition of highly concentrated (98.5% or greater) urea solution in essentially equal proportions to the APP melt permits production of 28-28-0 grade, generally considered a mix fertilizer. Increasing the proportion of urea permits production of a 35-17-0 grade. Although moisture content of material in the pugmill is increased by the return of scrubbing liquor, only cooling is required to produce granules of good quality. The polyphosphate content of these products ranges from 15 to 35%, and the moisture content is usually 1% or less. A diatomaceous earth

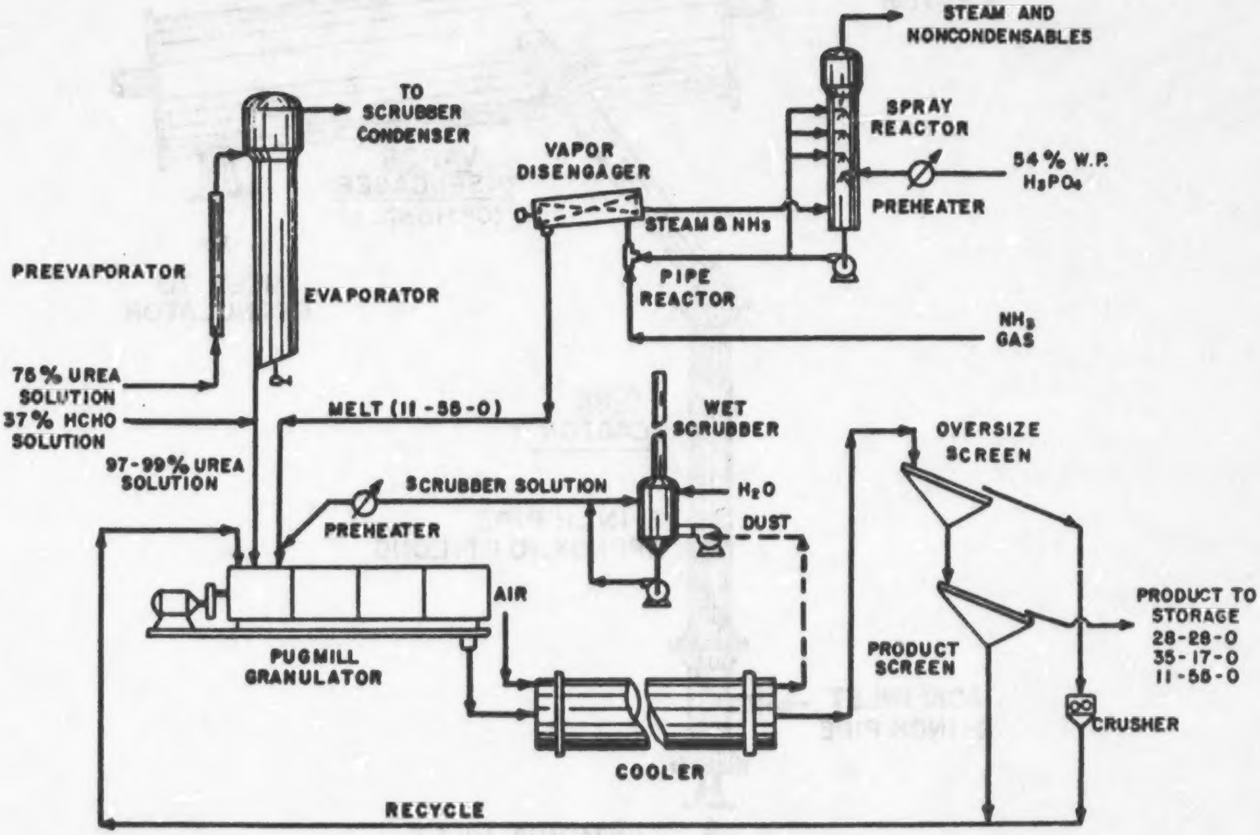

STEAM AND NONCONDENSABLES
TO SCRUBBER CONDENSER
SPRAY REACTOR
VAPOR DISENGAGER
54% W.P. H_3PO_4
PREHEATER
STEAM & NH_3
PIPE REACTOR
PREEVAPORATOR
EVAPORATOR
NH_3 GAS
75% UREA SOLUTION
37% HCHO SOLUTION
MELT (11-55-0)
WET SCRUBBER
OVERSIZE SCREEN
97-99% UREA SOLUTION
SCRUBBER SOLUTION
H_2O
PREHEATER
DUST
AIR
PRODUCT TO STORAGE
28-28-0
35-17-0
11-55-0
PUGMILL GRANULATOR
PRODUCT SCREEN
CRUSHER
COOLER
RECYCLE

Figure 26. Pipe-reactor/pugmill process.

Source: Parker, B.C., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipe-cross reactor. Paper presented at FAI-IFDC Seminar. New Delhi, India, 48 p.

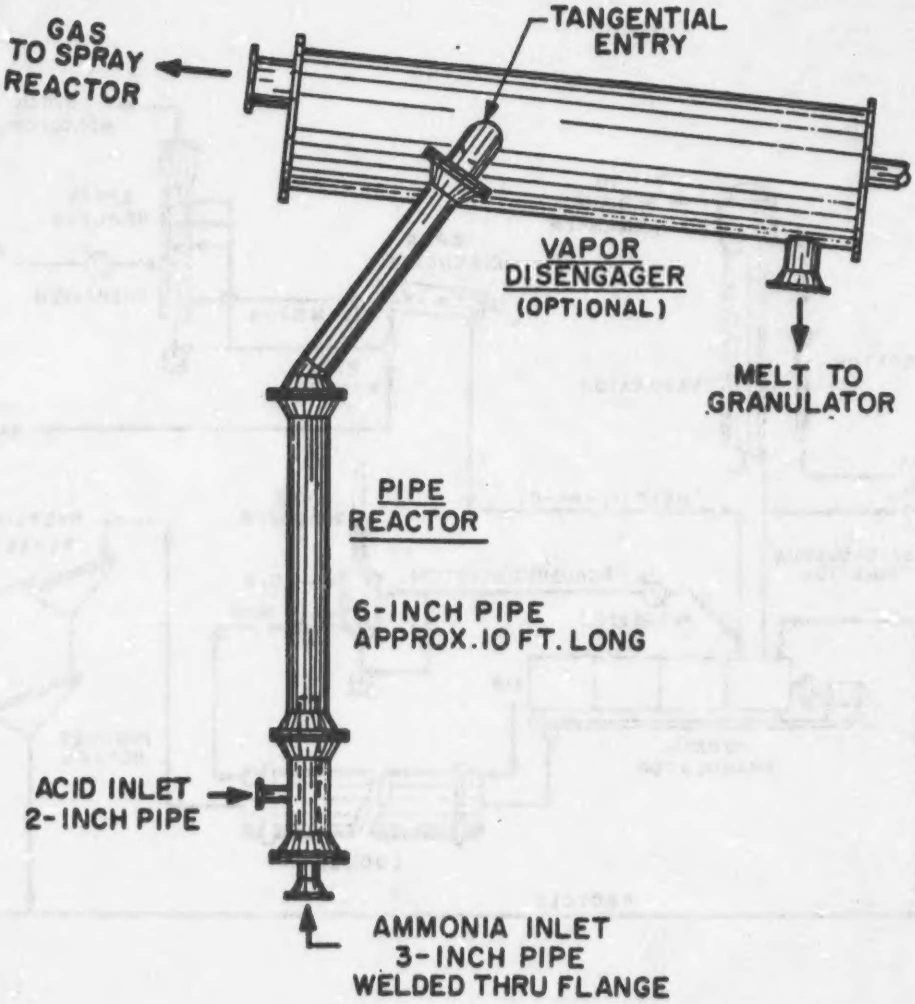

GAS
TO SPRAY
REACTOR
TANGENTIAL
ENTRY
VAPOR
DISENGAGER
(OPTIONAL)
MELT TO
GRANULATOR
PIPE
REACTOR
6-INCH PIPE
APPROX. 10 FT. LONG
ACID INLET
2-INCH PIPE
AMMONIA INLET
3-INCH PIPE
WELDED THRU FLANGE

Figure 27. Pipe reactor and vapor disengager.

Source: Parker, B.C., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipe-cross reactor. Paper presented at FAI-IFDC Seminar. New Delhi, India, 48 p.

or kaolin clay conditioner is needed for the 35-17-0 grade product (Parker et al 1977). Use of this system, which does not require a rotary dryer and related equipment has substantially reduced both capital and operating cost, thus accelerating its acceptance in both straight and mixed manufacturing facilities.

In 1974 TVA demonstrated the use of a drum granulator in a melt-type pipe reactor process (TVA 1974). This process has been widely accepted, especially since it eliminates the need for dryers in plants already equipped with conventional TVA ammoniator-granulators. Good granulation can be obtained without the mixing action of a pugmill by discharging the melt directly into a drum granulator through a perforated pipe (see Figure 25) rather than a single orifice. The melt is atomized by the steam that expands through the holes in the pipe. In this process the size and number of holes are adjusted so that a pressure of 10 to 15 psig is maintained. Obviously, the presence of a small amount of water in the melt is now turned to beneficial use, atomizing the melt. In addition, the rotary vapor disengager is eliminated. Several NP and NPK formulations and MAP have been produced with this process, which is less expensive to operate and somewhat more energy efficient than the pugmill pipe reactor process because the rotary drum requires less horsepower to drive.

Figure 28 is a flowsheet of a modified version of the pipe-reactor/drum-granulator process in which a preneutralizer is not used. This simplifies the process considerably because a major piece of equipment and its related piping, transfer and metering equipment, and scrubbing system are not needed. 11-55-0 MAP (5% polyphosphate) produced using this process compares favorably with that of the process using a preneutralizer. With this process, both investment and operating cost are significantly lower because of the equipment eliminated.

Pipe-Cross Reactor

In 1974, TVA in cooperation with the Missouri Farmers Association developed a modification of the pipe reactor in which a pipe cross instead of a pipe tee is used to allow for the introduction of a second acid (sulfuric acid usually) in addition to phosphoric acid and ammonia. This reactor, called a pipe-cross

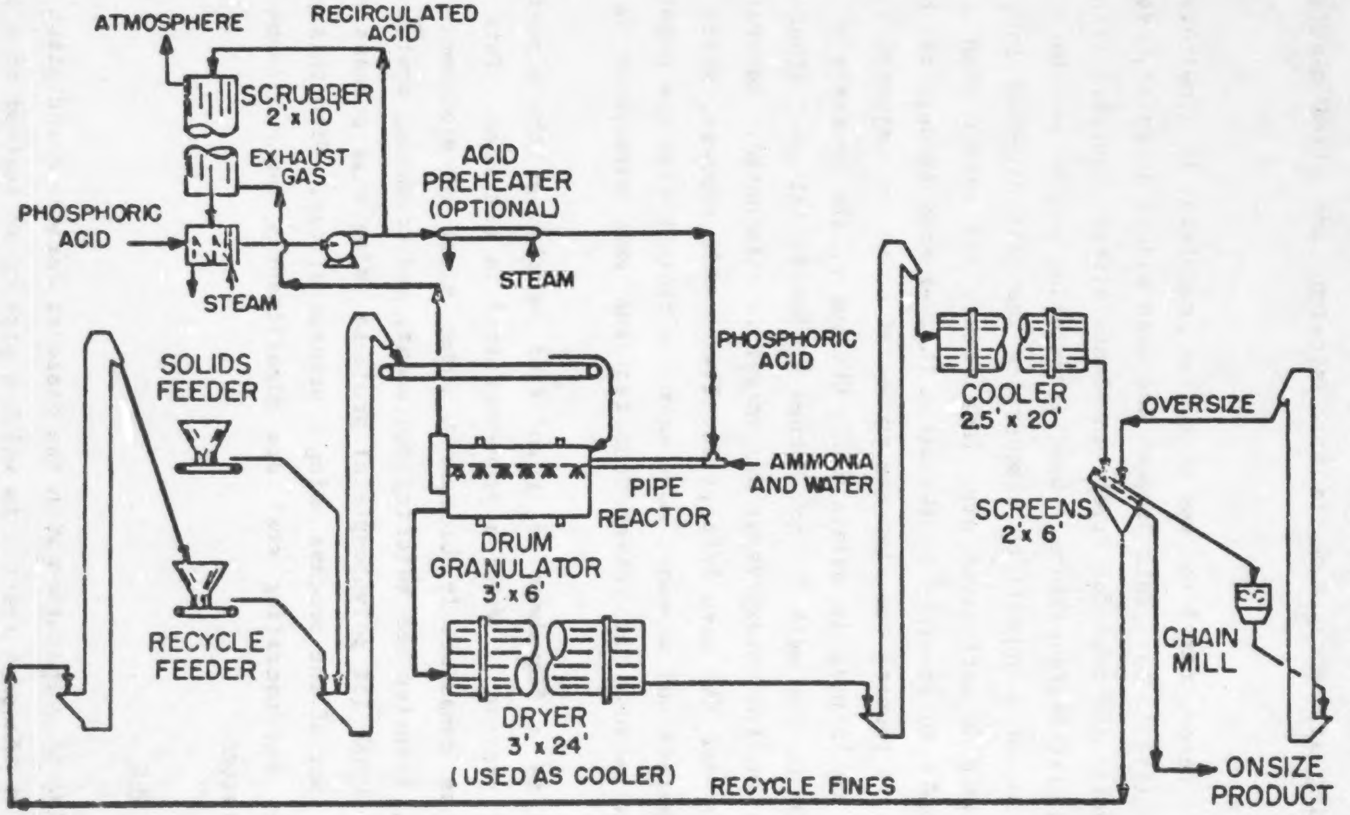

ATMOSPHERE
RECIRCULATED ACID
SCRUBBER 2' x 10'
EXHAUST GAS
PHOSPHORIC ACID
STEAM
ACID PREHEATER (OPTIONAL)
STEAM
SOLIDS FEEDER
RECYCLE FEEDER
PHOSPHORIC ACID
AMMONIA AND WATER
PIPE REACTOR
DRUM GRANULATOR 3' x 6'
DRYER 3' x 24' (USED AS COOLER)
COOLER 2.5' x 20'
OVERSIZE
SCREENS 2' x 6'
CHAIN MILL
ONSIZE PRODUCT
RECYCLE FINES

Figure 28. Pipe-reactor/drum-granulator process without a preneutralizer.

Source: Parker, B.C., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipecross reactor. Paper presented at FAI-IFDC Seminar. New Delhi, India, 48 p.

reactor (Figure 29) has proved very successful in the production of NP and NPK grades of granular fertilizers that require little or no drying. Although NPK formulations have been predominant, MAP has also been produced commercially. The preneutralizer is also eliminated when the pipe cross reactor is used (Achorn and Kimbrough in TVA 1978a). Grades such as 12-48-0, 12-12-12, 6-24-24, 8-22-11, 10-40-10, 20-10-10, 17-17-17, 33-11-0, and 18-46-0 have been produced either in commercial plants or in TVA's pilot plant. Several pipe-cross reactors are in commercial operation, and others are planned. TVA is continuing pilot-plant studies of the process to further refine variables and operating conditions for various grades (L. B. Nelson in TVA 1978a). Figure 30 shows a typical ammoniation-granulation plant in which MAP, NP, and NPK formulations can all be produced.

In addition to the advantages already described for a pipe reactor without preneutralizer the pipe cross reactor offers additional benefits (Parker et al. 1977):

1. Larger amounts of acid, both phosphoric and sulfuric, can be used in formulations.

2. There is less formation of troublesome ammonium chloride fume which is difficult to scrub from exhaust gases.

3. Moisture content of the slurry or melt produced is lower and there is a more favorable moisture balance in the process.

4. Granular MAP, which is an excellent product for blending, can be produced more conveniently; a wider range of grades can be blended with MAP (12-48-0 or 11-55-0) than with DAP (18-46-0).

Non-TVA Commercial Processes

A number of other processes for production of ammonium phosphate are in use in the United States. The Fisons process and the Swift process utilize mixing nozzles and the Gardinier process utilizes an all-in-one reactor-mixer-spray nozzle. These processes spray the resulting melt or slurry into the top

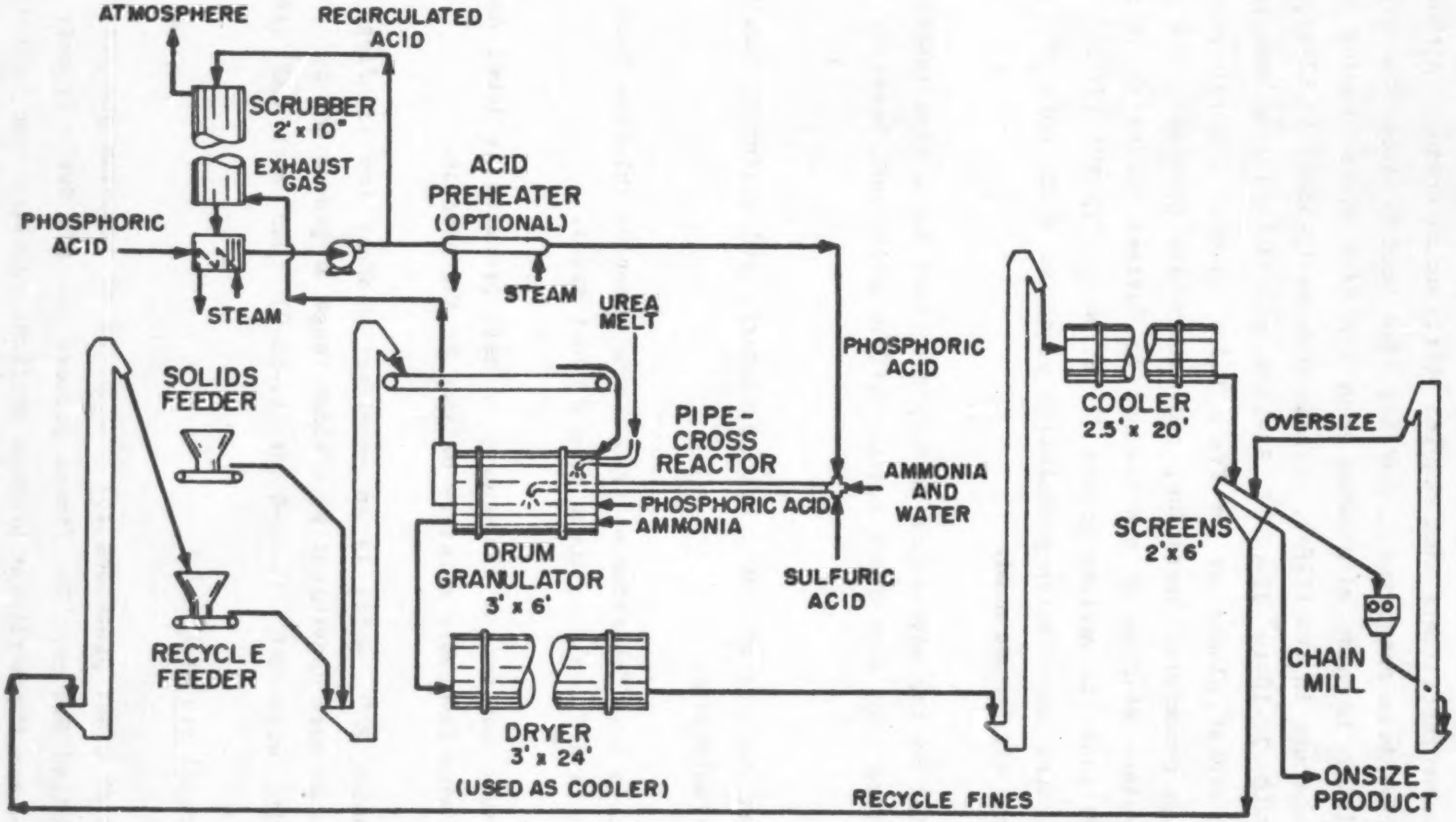

ATMOSPHERE
RECIRCULATED ACID
SCRUBBER 2'x10"
EXHAUST GAS
ACID PREHEATER (OPTIONAL)
PHOSPHORIC ACID
STEAM
STEAM
UREA MELT
SOLIDS FEEDER
PIPE-CROSS REACTOR
PHOSPHORIC ACID
AMMONIA AND WATER
PHOSPHORIC ACID
AMMONIA
DRUM GRANULATOR 3' x 6'
SULFURIC ACID
RECYCLE FEEDER
DRYER 3' x 24' (USED AS COOLER)
COOLER 2.5' x 20'
OVERSIZE
SCREENS 2'x6'
CHAIN MILL
ONSIZE PRODUCT
RECYCLE FINES

Figure 29. Pipe-cross reactor/drum-granulator process.

Source: Parker, B.C., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipecross reactor. Paper presented at FAI-IFDC Seminar. New Delhi, India, 48 p.

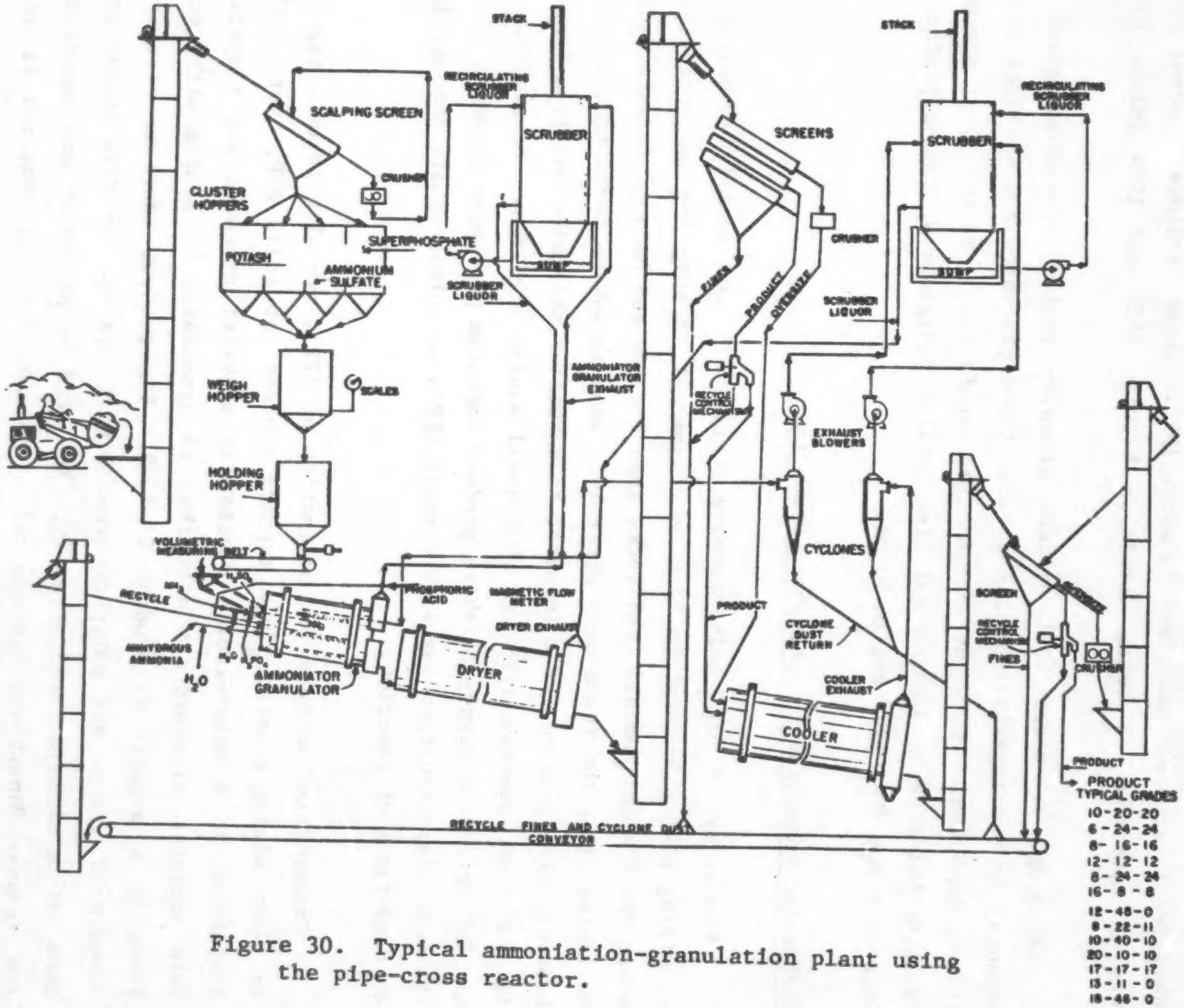

STACK
RECIRCULATING SCRUBBER LIQUOR
SCALPING SCREEN
SCRUBBER
CRUSHER
CLUSTER HOPPERS
SUPERPHOSPHATE
POTASH
AMMONIUM SULFATE
SUMP
SCRUBBER LIQUOR
WEIGH HOPPER
SCALES
HOLDING HOPPER
AMMONIATOR GRANULATOR EXHAUST
VOLUMETRIC MEASURING BELT
NH_3
H_2SO_4
RECYCLE
ANHYDROUS AMMONIA
H_2O
H_2O
H_3PO_4
AMMONIATOR GRANULATOR
PHOSPHORIC ACID
MAGNETIC FLOW METER
DRYER EXHAUST
DRYER
SCREENS
FINES
PRODUCT
OVERSIZE
CRUSHER
RECYCLE CONTROL MECHANISM
STACK
RECIRCULATING SCRUBBER LIQUOR
SCRUBBER
SUMP
SCRUBBER LIQUOR
EXHAUST BLOWERS
CYCLONES
PRODUCT
CYCLONE DUST RETURN
COOLER EXHAUST
COOLER
SCREEN
RECYCLE CONTROL MECHANISM
FINES
CRUSHER
PRODUCT
RECYCLE FINES AND CYCLONE DUST CONVEYOR
PRODUCT TYPICAL GRADES
10-20-20
6-24-24
8-16-16
12-12-12
8-24-24
16-8-8
12-48-0
8-22-11
10-40-10
20-10-10
17-17-17
13-11-0
18-46-0

Figure 30. Typical ammoniation-granulation plant using the pipe-cross reactor.

Source: Parker, B.C., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipe-cross reactor. Paper presented at FAI-IFDC Seminar, New Delhi, India, 48 p.

of a reaction tower where the droplets solidfy before reaching the bottom, with moisture contents of 2 to 6%. The ammonium phosphate produced is generally in a powdered or nonuniform semigranular form. In 1973 there were 15 Fison plants in operation or under construction. The Swift process was put into operation in at least one plant in about 1975. Three Gardinier process plants were in operation or being developed between 1972 and 1974 (Hicks 1977).

Although processes that produce granular product are advantageous and expected in new installations, the above three processes are included in this discussion because it is not uncommon for manufacturers to modify or add on to existing hardware to improve existing capital equipment or expand production. In such cases NSPS may have to be met.

Discussion--Ammonium Polyphosphate Production

Production of high polyphosphate fertilizers such as APP is usually done at mixing plants because it is more economical to ship and more practical to store the SPA and ammonia feedstocks than the APP and because formulations can be varied using the feedstocks directly. Some phosphate fertilizer complexes, however, also produce APP's in order to sequester magnesium and iron impurities in their wet process acid and thus avoid sludge problems. In addition, MAP and DAP processes discussed above produce ammonium phosphate products in which the molecular structure may also contain APP's as polyphosphate chains, depending on conditions of reaction.

Conventional methods for production of APP's are also in use, especially in older mixing plants. In a typical process for solid APP, thermal SPA is ammoniated in a water-cooled reactor at elevated pressure and temperature. This produces an anhydrous melt that is granulated by mixing with recycled fines in a pugmill to produce 27-34-0. The product contains nearly equal amounts of ortho- and polyphosphate (Dinauer 1971). An alternative process uses orthophosphoric acid directly. The acid is preheated and ammoniated in two stages. Conditions are controlled so that heat of reaction is used to cause the molecular dehydration required to form polyphosphate molecules. The resulting melt is then granulated by mixing it with cooled recycled material in a pugmill (Dinauer 1971).

A TVA process produces 15-62-0 grade APP from thermal SPA. The acid is neutralized in a cooled, pressurized reactor with anhydrous gaseous ammonia. The melt is granulated in a pugmill, cooled, and screened. Dust is collected by wet scrubbers and scrubber liquor is recycled into the acid feed. The product contains 75-80% of the P content as polyphosphate (Lee and Waggoner 1975). Such high concentrations are needed in some liquid fertilizers produced from the material in order to prevent precipitation of magnesium compounds (TVA 1974). This process produces granular product, but adding water in a final step produces a liquid for use as a base for liquid blend fertilizers.

Liquid APP is being produced in a large number of United States commercial plants by use of a TVA-developed pipe reactor which utilizes wet process superphosphoric acid (TVA 1974). In the past it has been difficult to produce satisfactory 10-34-0 and 11-37-0 liquid fertilizers from wet process SPA in a conventional tank reactor because the polyphosphate contents of the acid and products were less than desired. Because of impurities, wet process superphosphoric acid normally is too viscous to handle satisfactorily when it is concentrated to a range that provides much more than 50% of the P_2O_5 as polyphosphate. Liquids such as 11-37-0 require at least 65%, and 10-34-0 at least 50%, of their P_2O_5 as polyphosphates to prevent precipitation of ammonium phosphate for extended periods of storage at standard 80 F (27 C) or 32 F (0 C) temperatures. Still higher polyphosphate content of 75% to 80% is required to avoid precipitation of magnesium compounds. The pipe reactor process permits production of liquids containing much more polyphosphate than had been possible previously by conventional methods using wet process acid. An additional advantage of this process is that feed acid containing only 15% to 30% of the P_2O_5 as polyphosphate can be used. This acid is cheaper to produce and can be stored and handled more easily than acid containing about 50% polyphosphate, which was needed with prior technology.

In the TVA process, liquids containing from 70% to 80% of the P_2O_5 in polyphosphate form are produced from low-polyphosphate (15% to 30%) wet process superphosphoric feed acid. Also, either furnace or mixed superphosphoric acid (a mixture of electric-furnace superphosphoric acid and wet process orthophosphoric acid) can be successfully ammoniated simultaneously with wet process orthophosphoric acid to produce 11-37-0 of high-polyphosphate content. The high-polyphosphate process consists of reacting the acid with anhydrous gaseous ammonia in a simple pipe reactor. The heat of reaction results in temperatures of about 600° to 750° F and converts a large part of the orthophosphate contained in the feed acid to polyphosphates. The reaction product made at the high temperature is an anhydrous melt of about 10-62-0 grade with 70% to 80% of the P_2O_5 as polyphosphates. As shown in Figure 31, this melt is discharged continuously into the liquid fertilizer vessel where water and supplemental ammonia are added. The pH of the fluid is maintained at about 6 as the melt is dissolved. The fluid in the reaction vessel is maintained at about 150 F (66 C) by recirculation through a water-cooled heat exchanger (TVA 1974).

Ammonium phosphates have been the leading phosphate fertilizers produced in the United States since 1968. The process equipment for ammoniation-granulation usually has the capacity, or is easily modified, to include production of numerous NPK formulations. These process modifications are readily effected by adding in feed systems for granular or fine particulate potassium solid fertilizers or for nitrogen solids, such as granular urea. Sulfates are produced by adding in a sulfuric acid feedstream in the reaction system, often to take advantage of operating improvements it offers, such as reduction in scaling which occurs with phosphoric acid alone, or to increase polyphosphates content. APP's can be produced in the same process trains and most NPK products contain phosphorus in both orthophosphate and polyphosphate forms. Manufacturers appreciate the flexibility in NPK processes because they can change the product they are manufacturing in response to market demands, feedstock availability and profitibility, and to solve operational problems such as scaling or troublesome emissions. As discussed in Section 1.1, operations performed at such plants place them concurrently or at different periods in both phosphate fertilizer and mixed fertilizer subcateogries. For the most part APP's are produced at mixing plants, but the similarity in process equipment and formulations, and the inclusion of some APP-rich formulations in MAP production categories have tended to invalidate conventional categories.

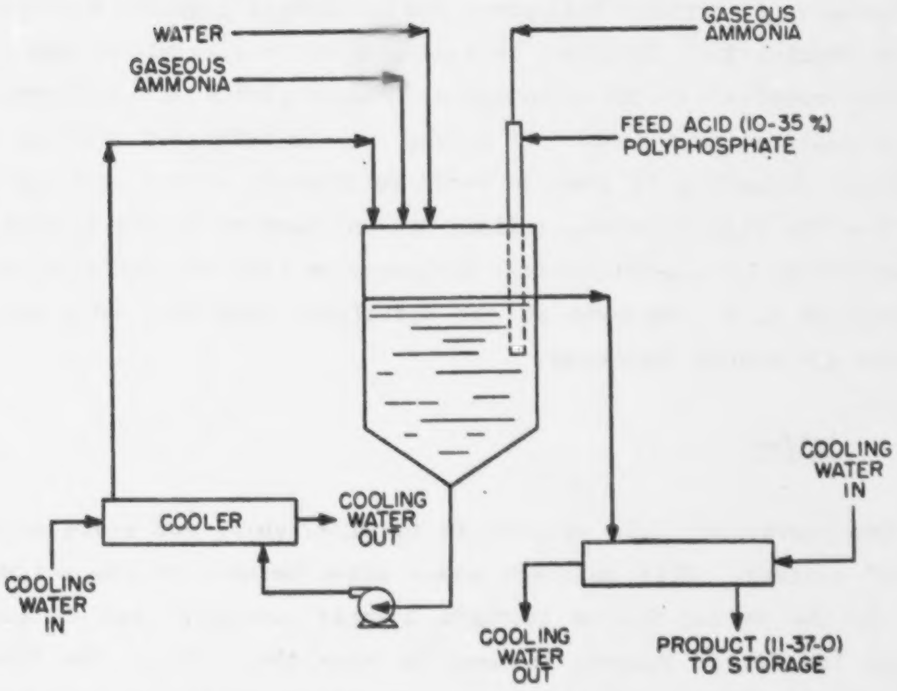

WATER
GASEOUS AMMONIA
GASEOUS AMMONIA
FEED ACID (10-35 %) POLYPHOSPHATE
COOLER
COOLING WATER OUT
COOLING WATER IN
COOLING WATER IN
COOLING WATER OUT
PRODUCT (11-37-0) TO STORAGE

Figure 31. Plant pipe reactor system for production of high-polyphosphate liquid fertilizer.

Source: Tennessee Valley Authority. 1974. New developments in fertilizer technology, 10th demonstration, October 1-2, 1974. National Fertilizer Development Center. Muscle Shoals AL, 72 p.

1.3.3 Auxiliary Support Systems

1.3.3.1 Raw Materials Transportation

Phosphate Rock

Phosphate fertilizer facilities generally receive ground phosphate rock concentrate by enclosed systems. Pneumatic systems are used for dry material (USEPA 1978d) and pipelines for slurries. Outdoor storage piles are built over systems of vertical feed pipes and horizontal conduits enclosing conveyors, so that feeding into the plant is done by gravity from within the storage pile and then moved in enclosed conduits. Other plants are delivered phosphate rock by railroad hopper car. If ground rock is delivered, covered hopper cars are used. Unloading is done in enclosed transfer areas, and enclosed elevators move the rock to storage silos. Exhaust systems in the transfer areas and storage silos are passed through baghouses to recover particulates. When wet grinding is to be employed at the fertilizer facility, rock can be shipped unground and stored uncovered.

Sulfur

The prevailing U.S. pattern is to mine, ship, and store sulfur in "all liquid" systems. This approach makes sense because of the volume of sulfur used in the United States (world's largest consumer) and is made feasible because the Frasch process is used to mine the sulfur. The Frasch process takes advantage of very pure massive deposits of sulfur in salt dome structures and in other structures along the Gulf Coast in Louisiana, Texas, and Mexico. In the Frasch process heated water and steam are injected into sulfur beds through jacketed concentric pipe casings, and sulfur melted by the process is withdrawn through an annular space in the casing. The Frasch process is energy intensive but viable, largely because of the advantages of transporting and handling sulfur in molten form in controlling air pollution and lessening equipment corrosion. Most uses require that sulfur feedstocks be melted for processing, so there is a partial payback of energy consumption at that stage.

The conversion to liquid handling systems in the United States began in the early 1960's (Carrington 1962). Consequently, multi-million dollar liquid sulfur transportation and handling networks are now well established. Phosphate fertilizer facilities receive Frasch sulfur by road and rail tankers, pipelines, bargelines, and ocean-going tankers. Transportation facilities and all pumps and tank terminals are equipped with insultation and heating equipment to maintain the sulfur at temperatures between 240 and 320 F (116-160 C) (Anonymous 1970).

Ammonia

Phosphate manufacturing utilizes ammonia for production of ammonium phosphates. Plants that do not produce ammonium phosphates would not use ammonia in significant quantities (58.45% of the phosphate straight fertilizers produced from wet process phosphoric acid are ammonium phosphates (USEPA 1974d)).

Ammonium phosphates are produced either at facilities near sources of phosphate rock or at facilities that produce ammonia or are nearby ammonia sources. Those facilities that produce ammonia require good sources of natural gas, and ammonia product is transported by in-plant pipelines and inventories stored at low temperatures (as low as -50 F or -46 C) in cryogenic tanks. Facilities which purchase ammonia receive shipments of compressed liquid anhydrous ammonia or aqua ammonia by barge or road or rail tanker (USEPA 1976b). Throughout the Midwest anhydrous ammonia is available (primarily to mixing plants) by pipeline networks. Ammonia storage tanks may be cryogenic. Modern ammonia terminal systems are also designed to deliver ammonia to pressure tanks at ambient temperatures.

1.3.3.2 Product Handling, Storage, and Transportation

Granular and ground solid products are handled, stored, and loaded for shipment using some of the same systems or similar systems used for phosphate rock (1.3.3.1). Loading is done by covered conveyors or from hoppers to barges, rail hopper cars, or trucks for shipment. Loading areas are usually enclosed or equipment and receiving vehicles are hooded during transfer. Materials that are handled using dry transfer facilities are product phosphate rock, NSP, TSP, and ammonium phosphates. Hopper cars are open, however, and can lose some dry products as particulates to the air or by spillover from overloaded hoppers.

Phosphoric acid and SPA require special materials for construction of storage tanks, pumps, and pipe-work that are strong, flexible, resistant to strong acids, and able to withstand temperature extremes. Details of selection of proper materials for process equipment or handling, storage, and transportation equipment is not a subject of this document. Spill and leakage prevention can be enhanced, however, by use of suitable materials such as certain stainless steel alloys, plastics, rubber, and fiberglass.

Phosphoric acid is delivered to tanks and transport vehicles through pipes and hoses made of the above materials. Phosphoric acid storage tanks may be flat-bottom or cone-bottom, and are usually constructed of a mild steel shell with rubber lining. When flat-bottom tanks are used, good design for leakage control includes construction of tanks on a concrete foundation elevated to keep the shell from coming in contact with any spilled acid. The foundation should have grooves (drain spokes) in its upper surface radiating toward the edges; this transmits any leaking acid from the tank base out from under the tank to minimize corrosion and allow easier detection (Barber 1975a). Cone-bottom tanks are used to facilitate removal of settled solids. Since removal pipes are at the bottom of cone-bottom tanks, the tanks are usually elevated on a supporting frame (Balay and Kimbrough 1978). Smaller tanks, for intermediate storage, are frequently of the horizontal cylindrical type; these are supported on concrete buttresses. All storage tanks are ideally surrounded by a diked-in area large enough to contain the contents of the largest tank (Barber 1975a).

Phosphoric acid is transported by rail or road tankers (USEPA 1978b). Superphosphoric acid from wet process acid presents special handling problems due to its high viscosity. This characteristic can be largely overcome by loading the acid at elevated temperatures in especially designed insulated tank cars known as "hot dog" cars. A stainless steel shell is surrounded by six inches of polyurethane foam and an outer carbon steel shell. Internal pipe coils are located around the bottom of the inner shell so that steam and hot water can be piped in to keep the SPA between 150 and 200 F (52-75 C). The storage tank and lines to the transfer area are also insulated (Balay and Achorn 1971).

1.3.3.3 Intake Water Treatment

The only process which requires water treatment is the boiler make-up water for the sulfuric acid process. Impurities which would scale and foul boilers are removed by hot lime-zeolite treatment. Raw water is heated by steam in this lime softening process and filtration is through zeolite filters and a final anthracite (coal) filter. Impurities are collected in the softener tank and released by sludge blowoff (USEPA 1974a, Drew Chemical Corp. 1977).

1.3.3.4 Uranium Recovery

There is a small amount of uranium in phosphate rock, and it is dissolved as part of the 32% acid in the wet-process system. In the 1950's there were three plants where solvent extraction units were operated commercially. All were plagued with operating difficulties, both in the uranium plant and in its effect on the phosphoric acid plant. None was economically successful and all were shut down in favor of more conventional methods of uranium processing (USEPA 1976b).

Currently there is a revival of interest in extraction of uranium as uranium oxide (yellow cake) because improvements have been made in extraction techniques and because the price of yellow cake has increased from $8 to $43 per pound since the early 1970's. Several plants in central Florida have experimentally recovered uranium from phosphoric acid, and commercial recovery is nearing reality. The most likely processes to be used involve liquid-liquid solvent extraction processes. Uranium Recovery Corporation (URC) in 1974-1975 installed a uranium recovery module consisting of two units, one at the phosphoric acid plant of W. R. Grace & Company near Bartow and the other at URC's central processing plant near Mulberry. The acid-plant unit has been involved in initial extraction and stripping, while the central-plant unit has been involved in final production of yellow cake (Engineering and Mining Journal 1975). International Minerals and Chemical Corporation (IMC) is developing a uranium recovery facility at its New Wales plant. The operation will utilize a two-cycle solvent extraction process using di(2-ethylhexyl) phosphoric acid plus trioctylphosphine oxide in kerosene (Interview, J. Allen, IMC, 16 August 1979).

The U.S. Energy Research and Development Administration (ERDA) estimated that more than 900 metric (1,000 short) tons of uranium oxide would be extracted in the study area by 1978; this would represent approximately 8 % of the total U. S. production for 1975 (USERDA 1976). Recent estimates from central Florida place uranium production at nearly 1500 short tons, about 10% of U. S. demand. Four chemical companies are currently involved in or setting up facilities for uranium extraction in Florida. This spin-off industry from the phosphate industry has been operated quasi-independently in several cases, as cooperative ventures between the phosphate company and the extracting company. At least one phosphate processing company has now begun operation of uranium extraction in their own facilities, and other phosphate complexes are expected to follow.

1.4 SIGNIFICANT ENVIRONMENTAL PROBLEMS

The discussion in this section is a brief summary of the major environmental considerations associated with phosphate fertilizer manufacturing facilities. More comprehensive treatment of industry impacts is developed in Chapters 2.0 through 6.0. Problems inherent with specified factors and materials are discussed even though environmental effects may normally be mitigated through process and control techniques. The intent is to identify potential significant problems which, as a minimum, new source EID's would be expected to address.

1.4.1 Raw Materials

Phosphate rock. Beneficiated rock has generated serious environmental problems in poorly controlled facilities. Dust can be a significant air contamination problem at each point of transfer of the materials and in the grinding process when dry grinding is used. A typical milling operation for rock grinding associated with a mining operation has the potential to contribute 7 grams of particulate per dry standard cubic meter of exhaust before emission control (USEPA 1978d). Mass emission rates for rock transfer systems were not sampled in the 1978 USEPA study, but visible emission measurements have shown that these systems can be operated with no visible exhaust.

Sulfur and Ammonia. These raw materials and their reaction products in the environment, have significant potential to contribute to pollution. Neither sulfur nor ammonia, however, as raw materials present significant problems to the environment. This is due largely to the efficient handling and transportation systems in use (1.3.3.1) and due to the expense of the materials and their obnoxiousness if spilled. Spills are rare and with the adequate recovery systems in use losses are held to a minimum.

1.4.2 Process-Related Problems

SO_2/SO_3 and Acid Mists. Gaseous oxides of sulfur are used in production of sulfuric acid from elemental sulfur. Uncontrolled, these emissions can exceed 46 kg/metric ton (103 lb/ton) of sulfuric acid produced (USEPA 1978b). Prior to the promulgation of NSPS in 1971 USEPA measured SO_2 emissions as high as 42.5 kg/metric ton (94 lb/ton) of 100% sulfuric acid. In addition, acid mist emissions uncontrolled can be as high as 3.7 kg/metric ton (9 lb/ton) of 100% acid. Oxides of sulfur and acid mists are also evolved in wet process phosphoric acid production, NSP, and TSP production. Acid mists in these processes include phosphoric acid, nitric acid, and fluosilicic acid.

Fluorine. Significant gaseous emissions of fluorine, including mists, are evolved in the processes for wet process phosphoric acid, SPA concentration, TSP, and ammonium phosphates. They are also evolved in NSP processes but have received less attention (no NSPS have been promulgated) because production of NSP is small relative to other phosphate fertilizer products.

A major source of fluorine pollution is the gypsum pond which most facilities use to contain solid wastes and act as a reservoir and settling pond for contaminated process water. Fluorides may be evolved from the gypsum ponds as volatile fluorine, hydrogen fluoride, and silicon tetrafluoride.

Particulate Air Emissions. Particulates can be generated in all processes in which phosphate rock is acidulated and in all processes in which a solid product is manufactured. Those processes with significant potential for particulate emissions are:

- wet process phosphoric acid production
- NSP production
- TSP production (especially nongranular)
- ammonium phosphates (nongranular)

Solid wastes from gypsum ponds and gypsum stacks have not proven to be a source of significant particulates.

Process Wastewater. If they were discharged regularly and untreated, process wastewaters would cause severe and long-lasting or permanent environmental damage to surface water ecosystems. New source facilities will be permitted to discharge only treated process wastewaters. Due to the costs of pretreatment and the requirements of NSPS, they will discharge only during wet weather or periods of water balance misadjustments, when the capacity of storage ponds might otherwise be exceeded. But the possibility of accidential or uncontrolled discharge cannot be ignored. The gypsum pond (from which any discharge would emanate) contains harmful pollutants including the following:

- phosphorus
- fluorides
- ammonia
- cadmium
- chromium
- zinc
- vanadium
- arsenic
- uranium
- radium-226
- sulfate

and significant levels of the following parameters:

- pH (extreme acidity, pH 1-2)
- suspended solids
- dissolved solids
- temperature

There is the possibility of environmental problems associated with contaminated wastewaters, even with no discharge, if seepage occurs through dikes and pond bottoms, thereby polluting surface- or groundwaters.

Solid Wastes. The major solid waste is gypsum, which is a by-product of wet process phosphoric acid production. The quantity of gypsum produced in a wet process plant ranges from 4.6 to 5.2 metric tons per ton of P_2O_5 produced. In volume, this translates to 1,360 cubic meters (1,779 cubic yards) yearly per metric ton of P_2O_5 produced per day. This is enough material to cover one acre 1.1 feet deep each year per each metric ton of P_2O_5 produced on a daily basis. A representative plant with only one process train produces 630 metric tons of P_2O_5.

Disposal is a major materials problem which can become a major pollution problem if improperly handled. Plants near the mine can dispose of some of the solid residue in mine pits; most others use gypsum ponds and piles. Rainfall runoff can cause serious ecological problems if suspended solids and phosphate and sulfate compounds are washed into surface streams and lakes. When rainfall drainage is controlled properly, the major concern remaining is for land use effects, due to the large amount of land used and its unsightliness.

In practice the disposition of waste gypsum rarely qualifies truly as disposal. Operators often refer to gypsum piles as "storage," and some consider the gypsum to be stockpiled for the future, when it might have an economic value. Some waste gypsum has been disposed of in mine pits very near plants, but this is a very minor portion of the total. Gypsum piles eventually fill available pits and are graded over original surface levels, to heights of 50-100 feet or more. No gypsum piles are known to have ever been retired because plant sites have been expanding or adding on throughout the history of phosphate fertilizer production rather than shutting down.

1.4.3 Pollution Control

There are no direct environmental problems brought about by pollution control methods. Air emissions technology removes fluorides and particulates from gaseous wastestreams and adds them to wastewater effluents. These increments are not considered a problem because wastewaters are not discharged. Ultimately, the additional fluorides and particulates (phosphate) and acids and other minor impurities collected in scrubber liquor become part of the solid waste disposal problem, but the quantities amount to insignificant increases.

An indirect environmental impact is a possible slight increase in fluoride emissions from gypsum ponds due to increased levels of fluorides from wet scrubbers. This is a minor increase which is outweighed by the beneficial effects of the original fluoride scrubbing.

The only aspect of pollution control which adversely affects the environment is the cumulative effects of improper maintenance of the equipment. Catalytic converters in sulfuric acid production are sometimes used when the catalytic beds should be replaced. In general, emissions control equipment capable of bettering standards of performance is usually serviced when the standards are being approached or exceeded. Scrubbers and precipitators sometimes break down or malfunction. The actual impact of these factors is not known.

1.4.4 Location

Ambient Air Quality. Ambient air quality is not generally a limiting factor. Phosphate fertilizer facilities are typically in areas of low population density and little other industrial development. Facilities in certain areas where natural gas and ammonia are produced are often in more industrially developed areas.

Hydrologic Regime. The ratio of rainfall to evaporation can be a major concern in maintenance of the plant water balance to meet requirements for no effluent discharge. Amount of rainfall, drainage properties, and depth to water table are of importance through their effects on efforts to control contamination of surface and groundwaters from gypsum disposal areas.

Soils and Geology. Plants which do not have suitable land to lay out or add on wastewater and solid waste disposal facilities have problems eliminating wastewater discharges and properly storing solid wastes. Unstable or weak soils and steep topography are elements of plant location that may limit the capacity to properly handle liquid and solid wastes.

1.5 TRENDS

1.5.1 Locational Trends

1.5.1.1 Geographic Trends

A distinction should be made between trends in phosphate fertilizers and trends in phosphate rock production. The phosphate fertilizers capacity in the United States is located about 30% on the Gulf Coast (Texas, Louisiana, Mississippi), about 50% in Florida, about 10% in the western states, and 10% scattered throughout the United States including North Carolina (Blouin and Davis 1975), with more than 80% of domestic production of phosphate rock being produced by Florida and North Carolina. The reason that the phosphate fertilizer production figure is significantly lower than proportionate rock production for Florida and North Carolina is that phosphate rock from those two states is exported to Gulf Coast states (while sulfur from the Gulf states is returned to Florida and North Carolina).

These geographic trends are expected to continue with substantial variations by individual products. For example, Figure 32 shows locations of phosphoric acid, TSP, ammonium phosphates, and anhydrous ammonia production facilities projected for 1980. Phosphoric acid plants are usually located at the phosphate rock source. In some cases they are located near sulfur when N-P grades are produced. Very few of the acid plants are market located.

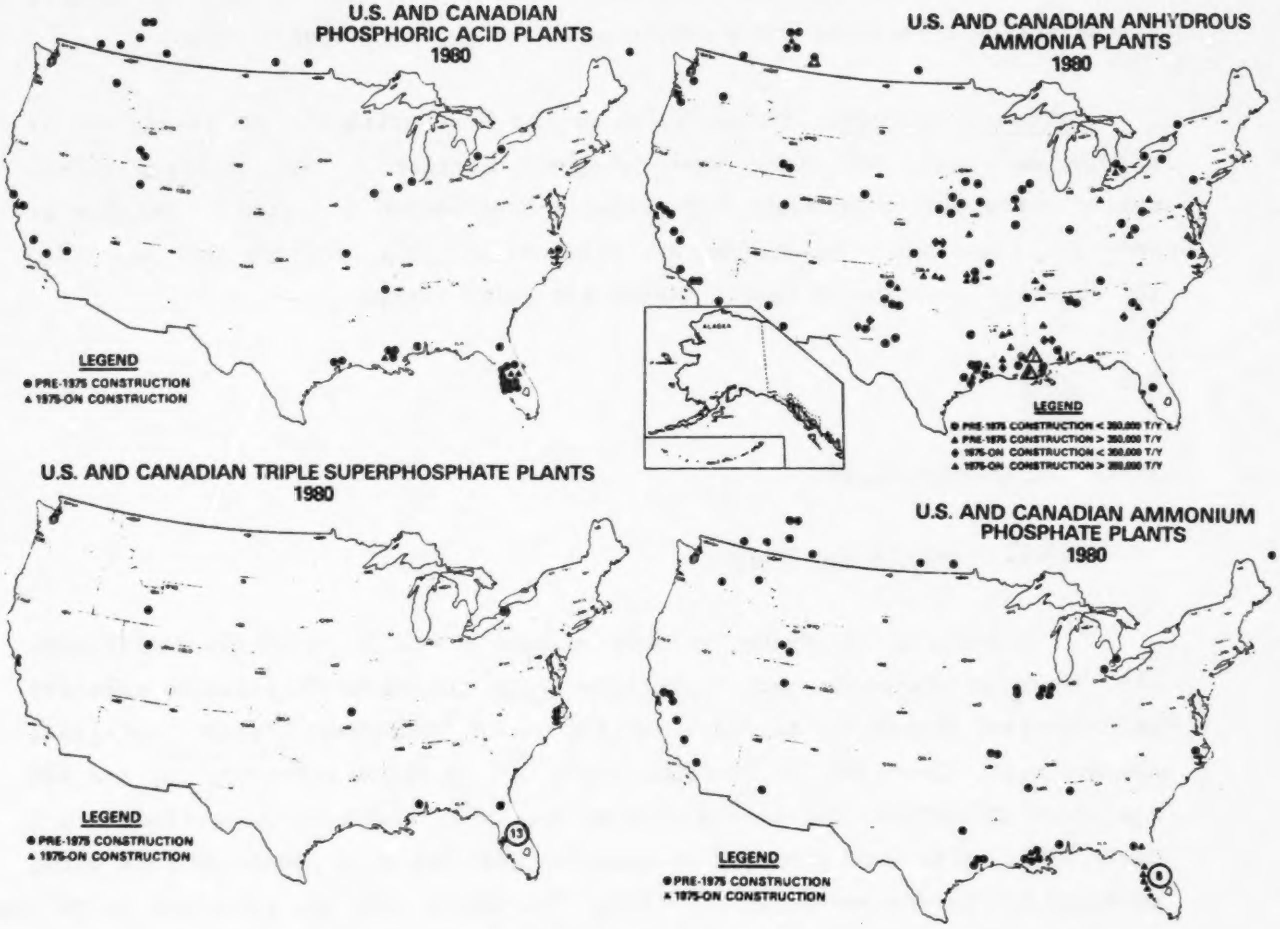

U.S. AND CANADIAN PHOSPHORIC ACID PLANTS 1980
LEGEND
● PRE-1975 CONSTRUCTION
▲ 1975-ON CONSTRUCTION
U.S. AND CANADIAN ANHYDROUS AMMONIA PLANTS 1980
ALASKA
LEGEND
● PRE-1975 CONSTRUCTION < 350,000 T/Y
▲ PRE-1975 CONSTRUCTION > 350,000 T/Y
◆ 1975-ON CONSTRUCTION < 350,000 T/Y
▲ 1975-ON CONSTRUCTION > 350,000 T/Y
U.S. AND CANADIAN TRIPLE SUPERPHOSPHATE PLANTS 1980
13
LEGEND
● PRE-1975 CONSTRUCTION
▲ 1975-ON CONSTRUCTION
U.S. AND CANADIAN AMMONIUM PHOSPHATE PLANTS 1980
8
LEGEND
● PRE-1975 CONSTRUCTION
▲ 1975-ON CONSTRUCTION

Figure 32. Locations of phosphate fertilizers and ammonia production.

Source: Adapted from Lyon, Fred D. 1976. Trends in storage, handling, and transport. Proceeding of TVA Fertilizer Conference, July 1976. Cincinnati OH, p. 37-42.

Triple superphosphate plants are located near phosphate rock deposits. These plants are also located next to phosphoric acid production so as to utilize sludge from acid operations. All but three are located close to navigable channels which provide a choice in mode of transportation.

Ammonium phosphates require phosphoric acid and ammonia. Most of the plants are located either at the phosphoric acid plant or at an ammonia facility. Only a few small plants are market located. Locations of anhydrous ammonia facilities illustrate the degree to which ammonium phosphates are being produced at these facilities (Lyon 1976).

After 1980, the production of mine-oriented materials should continue to follow the same pattern, with some production continuing in the Gulf Coast states, increased production in Florida through 1990, and substantially increasing production in North Carolina through the year 2000. The production in the western states will hold steady or increase slowly through the year 2000. The shipping advantages of concentrated materials such as SPA over phosphate rock should enforce the trend toward liquid fertilizers and result in a continuing increase in ammonium phosphate plants located near ammonia facilities and inexpensive transportation such as pipelines and bargelines.

In Florida the majority of the mining is done in the Central Florida District east of Tampa Bay. Polk County is the site of most of the current mining and fertilizer production, with several phosphate chemical plants in operation in Hillsborough and Manatee Counties. Planned mining and phosphate production facilities will be built in Hillsborough, Manatee, Hardee, and DeSoto Counties as the richer Polk County deposits are depleted (USEPA 1978i). In addition, less extensive deposits are being mined in North Florida.

1.5.1.2 Siting Trends

In Florida, where the majority of phosphate production will take place over the next 20 years, facilities will be close to mines. Many of the older facilities will be continued, but new facilities will be located in new mining areas in Hillsborough, Manatee, Hardee, and DeSoto Counties, and in North Florida.

In North Carolina, increasing production will entail new plant capacity in the Beaufort County mining area. Phosphate fertilizer plants will continue to be close to mines to take advantage of slurry transport systems. (Note: some operators have determined that dry transportation of rock by conveyors to beneficiation and processing plants may be economically competitive or advantageous for their locations, and these will be used by some plants.)

In general, siting of phosphoric acid production at sulfur and nitrogen producing facilities will continue. With United States demand for sulfur growing, it is likely that some new sulfur production capacity will incorporate phosphoric acid processes into the facilities. Siting of ammonium phosphate production will be concentrated in Florida complexes but with a greater percentage at ammonia producing plants on the Gulf Coast and in the midwest, and at blending plants along ammonia pipelines and barge systems.

The majority of production of phosphate products will be done at sites which are complexes for production of more than one product. 84.7% of basic fertilizers are produced in such complexes. Very few manufacturers are totally dependent on fertilizer production. Many are subsidiaries of chemical or petrochemical manufacturers, pipeline companies, steel manufacturers, or are run by a farm cooperative or a sulfur producing company. Siting may be at a complex where other materials are produced in completely separate or integrated process trains. The overriding trend in siting is toward large complexes. Economically, it is more profitable to operate a larger complex per ton of product. Capital investment per ton decreases in larger complexes, and pollution control costs per ton of P_2O_5 are lower in a 1,500 ton per day phosphoric acid plant than in one producing 500 tons per day.

1.5.2 Trends In Raw Materials

1.5.2.1 Sulfur

In 1975 consumption of sulfur in fertilizer production was 6.6 million long tons. Of that, 6.1 million (92%) was used in phosphate fertilizers. By 1985, the projected consumption of sulfur in the United States is 15.1 million long tons, with 9.3 million projected for fertilizer use. The trend is for more use of recovered and by-product sulfur. Data projecting sulfur-supply patterns are summarized in Table 13 (Douglas and Davis 1977).

These changes are not expected to have significant effects on fertilizer production technology. If economically feasible technology is developed to recover sulfur from high and medium-sulfur coals burnt in electrical power plants, this source is expected to become a significant factor by the late 1980's (Douglas and Davis 1977).

Table 13. Supply pattern for sulfur in the United States

Source	Estimated Production (long tons sulfur equivalent)	
	1975	1985
Frasch	7.8	8.2
Recovered		
Refinery	1.7	4.0
Sour gas	1.2	3.6
By-product sulfuric acid		
Nonferrous smelters	1.0	2.0
Stack-gas cleanup	-	0.6
Pyrites-based sulfur acid	0.4	0.5
Other	0.1	0.2
Total	12.1	19.0

Source: Douglas, John R. and Charles H. Davis. 1977. Fertilizer supply and demand. Chemical Engineering 84(15):88-94.

1.5.2.2 Phosphate Rock

Research is ongoing to develop technology to allow use of lower grades of rock (TVA 1978b). Use of somewhat lower grades in Florida has already begun, with the consequence that MAP has become more popular with basic producers of ammonium phosphates because rock with lower P_2O_5 content can be used which are difficult to use for production of 18-46-0 DAP (Nelson 1978). Expansion of the Central Florida Phosphate District is expected during the 1980's into counties surrounding Polk County, which will be using lower grades of phosphate rock (USEPA 1978b). Techniques under development to extract calcite and dolomite from phosphate rock, along with the current production of high polyphosphate liquid base solutions from high iron and magnesium North Carolina ores, point to a continuing trend to utilize phosphate rock sources previously considered too low in purity or P_2O_5 analysis.

1.5.2.3 Ammonia

Ammonia production currently uses natural gas as a feedstock, of which the United States has only a 10-year proven reserve. Natural gas is expected to remain important over the next decade, but developing efficient United States technology to make ammonia from coal has been widely identified as the number one national research priority for food production.

1.5.3 Process Trends

Processes are described in detail in Section 1.3. This discussion is a summary of the important process trends that are expected to be used in new source facilities and in upgraded existing facilities where they can be adopted.

Sulfuric Acid Production. The double absorption process has gained wide acceptance and is expected to become the standard because it allows achievement of NSPS for sulfur oxides. Of 32 new units completed since issuance of the NSPS only three have not adopted double absorption.

Phosphate Rock Processing. A trend is anticipated to wet grinding of phosphate rock. Wet grinding reduces particulate emissions and eliminates the energy-consuming step of drying the beneficiated rock. It is not known whether facilities that purchase (dried) rock plan to utilize wet grinding. Although not yet in commercial operation, small pilot projects to produce phosphoric acid directly from ground unbeneficiated rock have proven relatively encouraging; this procedure offers the potential to recover some of the phosphate content now lost in clay slimes and to reduce the production of slime ponds, currently a major land use problem at mining facilities (White et al. 1978).

Normal Superphosphate Production. Due to its low analysis, competition from other fertilizer products, and transportation costs of the phosphate rock feedstock, production is expected to decline slowly and reach a maintainable level of about 5% of total processed straight phosphate direct application materials. This production will be done primarily in small plants in the market areas.

Wet Process Phosphoric Acid. There are no new trends - sulfuric acid acidulation is the standard. Auxiliary processes for recovery of uranium oxide are expected as add-on process loops during acid production and purification steps. These involve solvent extraction instead of or in addition to clarification by settling.

Clarification of Phosphoric Acid. The use of settling and gravity precipitation techniques should continue. Use of solvent extraction techniques is not popular in the United States except in connection with uranium recovery, once the phosphoric acid has been produced. Use of lower grade ores with higher impurities may result in greater interest in solvent extraction in the mid-to late 1980's.

Superphosphoric Acid Production. Industry units are divided between submerged combustion and vacuum evaporation processes. The trend is to vacuum evaporation to avoid the drawbacks of submerged combustion, which require extensive scrubbing facilities due to the large volume of effluent gases.

Triple Superphosphate Production. The use of granulator processes is currently more popular and should continue. Nongranular forms are still produced largely for use as seed material in granulation-ammoniation processes. This practice may continue but is expected to decline further due to process modifications in ammoniation-granulation plants which use recycled fines and can use other fertilizer materials in granulation. Nongranular TSP is troublesome because of potential dust emissions at each handling stage; it is not wellsuited for dry blended fertilizers.

Ammonium Phosphate Production. DAP is popular and well-established. Its production levels are expected to trend downward, however, due to the difficulties in maintaining DAP formulations when lower analysis rock is used in production. MAP production is expected to regain marketing and production acceptance due to a number of reasons (Achorn & Kimbrough 1978):

1. Conventional DAP plants can produce MAP with exising equipment and at the same time eliminate one preneutralizer, reduce ammonia losses, and produce a lower moisture slurry that requires no drying.
2. MAP can be produced in a pipe-cross reactor with no preneutralizer.
3. MAP has more versatility for use by the bulk blender since a larger number of grades can be produced from MAP as compared to using DAP.
4. MAP is compatible with TSP whereas DAP reacts and causes caking when mixed with most commercially available TSP.
5. MAP can be used to produce suspension fertilizers by the addition of only ammonia whereas when DAP is used to produce these suspensions, phosphoric acid must be mixed with it and acid storage must be available at the dealer level.
6. The dual marketing of anhydrous ammonia and MAP is probably more economically attractive than ammonia and DAP.
7. Most phosphate producers desire to ship mostly P_2O_5 and add ammonia to the product only to convert the P_2O_5 to a suitable form for shipping.

1.5.4 Trends in Pollution Control

Pollution control systems and process designs are described in detail in Section 3.0. This discussion is a summary of the more widely adopted pollution control methods being integrated into new source facilities including upgraded existing facilities.

Wastewater treatment comprises a small segment of effluent control. Housekeeping, operational, and design controls are the foundations of wastewater effluent management. Control techniques which are expected include:

- Spill control and monitoring systems in sulfuric acid plants to contain, treat, and recycle spills and leaks.

- Elimination of discharge during normal operations by achieving water balance within or among the process trains. Techniques to meet this criterion include:
    1. Use of contaminated water for dilution of sulfuric and phosphoric acid.
    2. Use of recycled contaminated water in wet scrubbers.
    3. Routing of condensed contaminated water from steam ejectors and barometric condensers to the gypsum pond.
    4. Sale of scrubber liquor for fertilizer or fluorine recovery.
- Use of surface drainage systems to pass washdown and runoff waters to the contaminated gypsum pond.
- Design of gypsum ponds to contain specified rainfall events.
- Double-lime treatment of controlled discharge from gypsum ponds during rainfall events that exceed design capacities.
- Design and siting of gypsum ponds to control seepage and recycle collected seepage back to the pond.
- Control of NH_3-N loading to the gypsum pond by use of self-contained systems in the ammonium phosphate process to recycle or treat separately secondary wet scrubber liquor.

Control systems expected for gaseous emissions include pollutant control technologies and design modifications:

- Double absorption process modifications are usually chosen in sulfuric acid plants. Less popular techniques for new source facilities such as ammonia scrubbing, sodium sulfite-bisulfite scrubbing, and molecular sieves have experienced some operational or cost-related drawbacks.
- Use of acid mist eliminators; a number of systems are acceptable (Section 3.1).
- Use of baghouse filters and efficiently designed vent and circulation systems for capture and recycling of captured emissions.
- Use of enclosed dry material transfer and handling systems.
- Use of continuous process mills in NSP and TSP production with scrubbing and recycling of emissions.
- Use of pipe reactors and pipe-cross reactors in granulated fertilizer production, with the evolution of less ammonia (eliminating preneutralizers) and of lower particulate emissions.

Trends which attenuate the production of solid wastes include:

- Recycling of acid sludge to the phosphoric acid evaporator feed tank (USEPA 1979a).
- Production of SPA from high iron and magnesium phosphoric acid to sequester impurities in solution. This product can be used most readily in liquid fertilizers.

1.5.5 Environmental Impact Trends

1.5.5.1 Water Quality

Surface water contamination in phosphate processing drainage areas has been significant in the past. Untreated discharges from gypsum ponds are characterized by heavy loadings of sediment (suspended filterable solids), inorganic phosphorus, and fluorides.

Since promulgation of effluent guidelines for the phosphate fertilizer industry in 1974 regular discharge of gypsum pond effluents have been largely eliminated. Seepages and accidental discharges still occur and some existing sources have not completely discontinued regular discharges that will be prohibited in 1984. New sources constructed since 1974 and most phosphate fertilizer plants in operation have eliminated regular discharges. Table 14 is a summary of the results of a survey completed by Monsanto Research Corporation in 1976 and 1977 for the USEPA Industrial Environmental Research Laboratory (USEPA 1979a).

Definitive time series data are not available to compare baseline (pre-effluent guidelines) and present water quality. It is presumed that the trend to fewer discharges with specified limits on contaminant concentrations is a basis for a trend to less serious water pollution problems currently, and in the future.

The potential for groundwater contamination is based on an assemblage of variables including permeability of soils underlying gypsum ponds, effective gypsum pond bottom sealing and seepage control, and depth to water table. A study by the USEPA Office of Radiation Programs completed in October 1977

Table 14. Water effluent disposal and containment practices for the phosphate fertilizer industry.

	Industry					
	Wet process phosphoric acid plants	Superphosphoric acid plants	Normal superphosphate plants	Triple superphosphate plants	Ammonium phosphate plants	Total phosphate fertilizer industry
Process water discharged continuously:						
Treated	7 (2)[a]	0 (0)	0 (0)[b]	7 (1)[a]	6 (2)[a]	3.1 (2)
Untreated	3 (1)[c]	0 (0)	0 (0)	0 (0)	0 (0)	1.5 (1)
Discharge of treated process water only when necessitated by excessive rainfall[d,e]	38 (11)[f]	44 (4)[f]	6 (2)	57 (8)[f]	38 (12)[f]	18.5 (12)
No discharge of process water reported	52 (15)	56 (5)	88 (27)	36 (5)	53 (17)	72.3 (47)
Insufficient information	0 (0)	0 (0)	6 (2)	0 (0)	3 (1)	4.6 (3)
Total	100 (29)	100 (9)	100 (31)	100 (14)	100 (32)	100 (65)
Pond system onsite for water containment and reuse:	90 (26)	89 (8)	36 (11)	100 (14)	84 (27)	
Continuous discharge from pond system	7 (2)[a]	0 (0)	0 (0)	7 (1)[a]	6 (2)[a]	
Discharge only when necessitated by periods of excessive rainfall	38 (11)	44 (4)	6 (2)	57 (8)	38 (12)	
No discharge from pond system reported	45 (13)	44 (4)	23 (7)	36 (5)	38 (12)	
Treat pond system with lime to precipitate fluorides and other contaminants	3 (1)	11 (1)	13 (4)	7 (1)	3 (1)	
Uncertain	0 (0)	0 (0)	6 (2)	0 (0)	3 (1)	
No pond system onsite	0 (0)	0 (0)	-[g]	0 (0)	3 (1)[h]	
Information regarding wastewater handling system incomplete	10 (3)	11 (1)	3 (1)	0 (0)	13 (4)	
Recover fluosilicic acid	28 (8)	0 (0)	61 (19)	0 (0)	0 (0)	
Number of plants contacted	29	9	51[i]	14	33[i]	
Number of plants in industry	36	9	66	16	48	
Percent of industry surveyed	81	100	77	88	69	

[a] Completion of proposed modifications to water recycle system in December 1977 at one plant will result in discharge of process wastewater only in event of excessive rainfall.

[b] One NSP plant that was found to discharge into a sewer system after neutralizing liquid wastes ceased production in 1975.

[c] One plant uses Mississippi River water on a once-through basis and discharges without treating (gypsum is impounded).

[d] Actual number may vary somewhat since some plants that report no discharge of process wastewater may in fact discharge in the event of an extremely rainy period.

[e] Many plants report no discharge of process wastewater necessary for 3 yr or more.

[f] One plant reported that excess water is double limed and sent to a mine for use and that no contaminated water will be allowed to enter navigable streams or public waters.

[g] Number of plants having no pond system onsite is uncertain, because NSP plants practicing fluorine recovery may still employ a small pond or reservoir.

[h] Ammonium phosphate production unit is located at a steel mill.

[i] Wastewater handling practices for those plants expected to close during 1976 or early 1977 were not included in survey.

Source: U.S. Environmental Protection Agency. 1979a. Source assessment: Phosphate fertilizer industry. Office of Research and Development, Washington, D.C. Prepared by Nyers, J.M., G.D. Rawlings, E.A. Mullen, C.M. Moscowitz, and R.B. Reznik, Monsanto Corp., Dayton, OH, 201 p.

indicates, with a number of qualifications regarding the variability of conditions and performance of individual plants, that there may be no major wide-spread groundwater contamination by radium-226 levels in gypsum ponds and effluents (USEPA 1977d). Studies of Florida groundwater, however, are complicated by some high natural background levels of radionuclides and by anomolous and incomplete data. Although exceedingly low percolation rates through compacted aged gypsum cake and the underlying clay-permeated sediments have been reported (Wissa 1977), some local contamination of the water table aquifer is occurring at some sites, near gypsum stacks and ponds (TRC 1979). It has not been demonstrated definitively whether migrations of radionuclides take place through gypsum pond bottoms nor what degree of sealing is effective.

1.5.5.2 Air Quality

Since sulfuric acid and phosphate fertilizer NSPS have been promulgated, emission levels for particulates, sulfur oxides, acid mists, and fluorides have mandated performance levels which can be attained using available technology to control plant process emissions. The phosphate rock segment of the chemical and fertilizer mineral industry was estimated to have contributed 44,276,000 metric tons of particulate emissions in 1975, or 39% of the total for all chemical and fertilizer production (USEPA 1978e). The above figures include the mining and beneficiation processes, but it is evident that particulates are a major potential emission source for fertilizer handling and processes. Fluorides are contributed to emission streams in volatile forms and as constituents of particulate emissions. The overall environmental trend is for lowered emissions of particulates, sulfur oxides, acid mists, and fluorides using control technologies. Gypsum ponds have long been posited as a major virtually uncontrolled source of fluoride emissions. Recent modeling by Environmental Science and Engineering for the USEPA Industrial Environmental Research Laboratory dispute the significance of volatile emissions and suggests that fugitive dust from gypsum piles and deposits have been inadvertently included in measurements of gypsum pond emissions (USEPA 1978c).

It is clear that the lowering of emissions of fluorides will not be effective until sources are defined and agreed on. Meanwhile, a general trend that can be agreed on is that fluoride emissions could ultimately be lowered effectively by removing them completely from the waste system as a salable product, fluosilicic acid (USEPA 1978c). There is a trend toward the recovery and sales option, but it is not overwhelming due to unfavorable economics in some areas and for some removal processes.

1.5.5.3 Physiographic Impacts

The major environmental effect of the industry on the quality of the land resources is the disruption of the topography caused by the accumulation of gypsum deposits and long term dedication of land areas to gypsum ponds. Unlike the case of phosphate mines, however, where vast areas have been mined and/or tied up in slime ponds, fertilizer plants themselves involve relatively smaller land areas. Past experience has been that these impacts are, however, equally long term in that no major plants, gypsum piles, or ponds have been totally retired or reclaimed.

1.6 POLLUTION CONTROL REGULATIONS

1.6.1 Water Pollution

The Federal Water Pollution Control Act (FWPCA) Amendments of 1972 (P.L. 92-500) established two major interrelated procedures for controlling industrial effluents from new sources, and specifically included phosphate manufacturing in the list of affected categories of sources. The principal mechanism for discharge regulation is the NPDES permit. The other provision is the new source performance standard. The Clean Water Act of 1977 (P.L. 95-217), which amends P.L. 92-500, made no change in these basic procedures.

The NPDES permit, authorized by Section 402 of FWPCA, prescribes the conditions under which effluents may be discharged to surface waters. The conditions applicable to new or expanded phosphate fertilizer manufacturing facilities will be in accordance with NSPS, adopted by USEPA pursuant to Section 306, and pretreatment standards promulgated to implement Section 307(b). Stricter effluent limitations may be applied on a site specific basis if required to achieve water quality standards.

The effluent NSPS promulgated for new sources in the Fertilizer Manufacturing Point Source, Phosphate Subcategory under 40 CFR 418 are shown in Table 15. "Calcium sulfate" in Table 15 refers to gypsum or other calcium sulfate solid materials, which normally include dihydrate, anhydrite, or hemihydrite.

In principle, phosphate fertilizer manufacturing facilities can discharge contaminated nonprocess wastewater, with pretreatment, to publicly owned treatment works (POTW). In practice, however, nonprocess wastewater is often either combined with process wastewater or treated separately and either discharged or, once treated to remove such constituents as cooling water treatment chemicals (zinc or chromium compounds, for example), may be combined with process wastewater.

The USEPA pretreatment regulations stipulate that certain POTW's categorized by size and influent characteristics develop POTW Pretreatment Programs. These programs are intended to prevent the introduction of pollutants by industrial users that would interfere with the operations of treatment works, would pass through treatment works, or would adversely affect opportunities to recycle and reclaim wastewaters and sludges.

Regardless of specific limitations required by the Pretreatment Programs, the regulations (40 CFR 403.5) state the following may not be introduced into a POTW:

- Pollutants which create a fire or explosion hazard in the POTW.
- Pollutants which will cause corrosive structural damage to the POTW, but in no case discharges with pH lower than 5.0, unless the works is specifically designed to accomodate such discharges.
- Solid or viscous pollutants in amounts which cause obstruction to the flow in sewers, or other interference with the operation of the POTW.
- Any pollutant, including oxygen demanding pollutants, released in a discharge or such volume or strength as to cause interference in the POTW.
- Heat in amounts which will inhibit biological activity in the POTW resulting in interference but in no case heat in such quantities that the temperature at the treatment works influent exceeds 40 C (104 F) unless the works is designed to accommodate such heat.

Table 15. Standards of performance for new sources for wastewater effluents.

The following standards of performance establish the quantity or quality of pollutants or pollutant properties which may be discharged by a new source subject to the provisions of this subpart:

(a) Subject to the provision of paragraphs (b) and (c) of this section, the following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the best available demonstrated control technology: there shall be no discharge of process wastewater pollutants to navigable waters (41 FR 20582, May 19, 1976).

(b) Process wastewater pollutants from a calcium sulfate storage pile runoff facility operated separately or in combination with a water recirculation system designed, constructed, and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event may be discharged, after treatment to the standards set forth in paragraph (c) below, whenever chronic or catastrophic precipitation events cause the water level to rise into the surge capacity. Process wastewater must be treated and discharged whenever the water level equals or exceeds the midpoint of the surge capacity (41 FR 20582, May 19, 1976).

(c) The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

Effluent Characteristic	Effluent Limitations (mg/l)	
	Maximum for any one day	Average of daily values for 30 consecutive days shall not exceed
Total Phosphorus (as P)	105	35
Fluoride	75	25
TSS	150	50

(42 FR 16140, March 25, 1977)

The total suspended solids limitation set forth in this paragraph shall be waived for process wastewater from a calcium sulfate storage pile runoff facility operated separately or in combination with a water recirculation system, which is chemically treated and then clarified or settled to meet the other pollutant limitations set forth in this paragraph (41 FR 20582, May 19, 1976).

Table 15 concluded.

(d) The concentration of pollutants discharged in contaminated nonprocess wastewater shall not exceed the values listed in the following table:

Effluent Characteristic	Effluent Limitations (mg/l) Maximum for any one day	Effluent Limitations (mg/l) Average of daily values for 30 consecutive days shall not exceed
Total Phosphorus (as P)	105	35
Fluoride	75	25

(41 FR 20582, May 19, 1976; 42 FR 16140, March 25, 1977)

The effluent guidelines listed above do not presently include standards for pH. Standards of 8.0 to 9.5 which were previously promulgated were remanded in 1976, but limitations on pH of 6-9 are generally set at the State level or as a condition of the NPDES permit.

The pretreatment standards promulgated for new sources in the phosphate subcategory are quoted below:

> The pretreatment standards under Section 307(c) of the Act for a source within the phosphate subcategory, which is a user of a publicly owned treatment works (and which would be a new source subject to Section 306 of the Act, if it were to discharge pollutants to the navigable waters), shall be the standard set forth in 40 CFR part 128, except that for the purpose of this section, 40 CFR 128, 133 shall be amended to read as follows:
> In addition to the prohibitions set forth in 40 CFR 128, 131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works shall be as follows: There shall be no discharge of process waste water pollutants (40 CFR 418.16).

Note: 40 CFR 128, Environmental Protection Agency Pretreatment Standards, were issued in the June 26, 1978 Federal Register as 40 CFR 403.

In addition, there is a restriction on thermal discharges that becomes effective in June 1981.

Since new sources discharging to POTW's do not require NPDES permits, they are not subject to NEPA under Section 511(c) of the Federal Water Pollution Control Act, as amended by the Clean Water Act of 1977.

NPDES permits also impose special conditions beyond the effluent limitations stipulated, such as schedules of compliance and treatment standards. Once facilities are constructed in conformance with all applicable standards of performance, however, they are relieved by Section 306(d) from meeting any more stringent standards of performance for 10 years or during the period of depreciation or amortization, whichever ends first. This guarantee does not extend, however, to toxic effluent standards adopted under Section 307(a), which can be added to the facility's NPDES permit when they are promulgated. Toxic pollutants thus far identified do not include phosphate-fertilizer-related substances. The process which would be most likely to be considered in future toxic standards are solvent extraction processes for uranium oxide.

Many states have qualified, as permitted by Public Law 92-500, to administer their own NPDES permit programs. The major difference in obtaining an NPDES permit through approved State programs vis-a-vis the Federal NPDES permit program is that the Act does not extend the NEPA environmental impact assessment requirements to State programs. It is likely that new facilities or major expansions of existing facilities will come under increased environmental review in the future. Because the scope of the implementing regulations varies considerably, current information on prevailing requirements should be obtained early in the planning process from permitting authorities in the appropriate jurisdiction.

1.6.2 Air Pollution

The Federal regulations applicable to the air emissions from phosphate fertilizer manufacturing facilities are promulgated under six industry subcategories. The NSPS for the Sulfuric Acid Subcategory apply to sulfur dioxide and acid mist. The NSPS for the other five subcategories - Wet Process Phosphoric Acid Plants, Superphosphoric Acid Plants, Triple Superphosphate Plants, Granular Triple Superphosphate Storage Facilities, and Diammonium Phosphate Plants - apply to emissions of fluorine and all fluoride compounds (total fluorides).

The NSPS for the applicable subcategories are shown in Table 16. The standards for sulfuric acid plants, although promulgated, have been involved in lengthy litigations and have been virtually non-effective. A review of the standards was completed in August 1978 (USEPA 1978a) which has recommended that no revisions be made to the NSPS for sulfur dioxide or acid mists. Some states have, however, adopted stricter standards, although some of them apply

Table 16. New source performance standards for emissions of air pollutants from sulfuric acid plants and phosphate fertilizer manufacturing facilities.

Process	Standard
Sulfuric Acid Plants	Sulfur dioxide: 2kg/metric ton (4 lb/ton) of 100% H_2SO_4 produced.
	Acid Mist: (1) No more than 0.075 kg/metric ton (1.15 lb/ton) of 100% H_2SO_4 produced. (2) Not to equal or exceed 10% opacity.
Wet Process Phosphoric Acid Plants	Total fluorides: Not to exceed 10.0 g/metric ton of equivalent P_2O_5 feed (0.020 lb/ton)
Superphosphoric Acid Plants	Total fluorides: Not to exceed 5.0 g/metric ton of equivalent P_2O_5 feed (0.010 lb/ton)
Diammonium Phosphate Plants	Total fluorides: Not to exceed 30 g/metric ton or equivalent P_2O_5 feed (0.060 lb/ton)
Triple Superphosphate Plants	Total fluorides: Not to exceed 100 g/metric ton of equivalent P_2O_5 feed (0.20 lb/ton)
Granular Triple Superphosphate Storage Facilities	Total fluorides: Not to exceed 0.25 g/hr/metric ton of equivalent P_2O_5 stored (5.0×10^{-4} lb/hr/ton)

Sources: 40 CFR Part 60, 40 CFR Part 422.

only to specific industries or only to combustion sources. The applicability of these standards should be clarified when considering the impact of any new source.

It is possible that the Federal sulfur dioxide ambient air quality standards (40 CFR Part 50), which are nonenforceable goals for acceptable levels of this pollutant, may be exceeded in the vicinity of phosphate fertilizer facilities. Depending on site-specific operations, ambient air standards for particulates could be violated by many types of operations in this industry, especially in processing and handling phosphate rock and dry phosphate fertilizer products. Standards for sulfur dioxide and particulates are shown in Table 17.

Table 17. Federal ambient air quality standards.

Sulfur Dioxide	$(\mu g/m^3)$
Primary standard:	
Annual arithmetic mean	80
Maximum 24-hour concentration not to be exceeded more than once a year	365
Secondary standard:	
Maximum 3-hour concentration not to be exceeded more than once a year	1,300
Particulates	
Primary standard:	
Annual geometric mean	75
Maximum 24-hour concentration not to be exceeded more than once a year	260
Secondary standard:	
Annual geometric mean	60

SOURCE: 40 CFR Part 50.

Sulfuric acid plants or phosphate rock processing facilities with the capacity to emit 100 tons (91 kkg, or metric tons) or more per year of any air pollutant may be prohibited from constructing new facilities in certain areas under the Clean Air Act (P.L. 95-95) Prevention of Significant Deterioration (PSD) regulations. Also, any facility (which would include plants which react phosphoric acid but do not actually process phosphate rock) with the potential to emit 250 tons (227 kkg) or more per year of any pollutant may be prohibited from constructing new facilities in certain areas. Alternately, facilities in either of these two categories could be required to meet stricter air quality goals than the ambient air standards in other areas. The Clean Air Act Amendments of 1977 (P.L. 95-95) establish three types of areas to which PSD regulations may apply:

- Class I areas, in which almost any deterioration of air quality is deemed significant.
- Class II areas, in which a moderate increase in pollution concentration is acceptable, to allow for moderate growth.
- Class III areas, in which a greater pollutant increase is acceptable.

Increases in pollutant concentrations over baseline values are limited in these areas to those shown in Table 18. The allowable increments are limited to those which will not cause violations of the ambient air quality standards. The PSD program requires preconstruction approval of all new sources with significant potential emissions of SO_2 or particulate matter. Applicants for construction permits must demonstrate by monitoring and submission of air quality data that the new facility will not violate an applicable NSPS or increment or any air quality standard.

All international parks, national wilderness areas, and national memorial parks that exceed 5,000 acres, and all national parks that exceed 6,000 acres are classified as Class I areas. However, an exception may be granted to a source exceeding the Class I allowable increase on these mandatory Class I areas if a Federal land manager certifies that the facility will have no adverse impact on the air quality-related values, including visibility. In such cases, the allowable increases listed in the last column of Table 18 apply.

Table 18. Nondeterioration increments for SO_2 and particulate matter in areas with different air quality classifications.

Pollutant	Class I ($\mu g/m^3$)	Class II ($\mu g/m^3$)	Class III ($\mu g/m^3$)	Class I exception ($\mu g/m^3$)
Particulate matter:				
Annual geometric mean	5	19	37	19
24-hour maximum	10	37	75	37
Sulfur dioxide:				
Annual arithmetic mean	2	20	40	20
24-hour maximum	5*	91	182	91
3-hour maximum	25*	512	700	325

*A variance may be allowed to exceed each of these increments on 18 days per year, subject to limiting 24-hour increments of 36 $\mu g/m^3$ for low terrain and 62 $\mu g/m^3$ for high terrain and 3-hour increments of 130 $\mu g/m^3$ for low terrain and 221 $\mu g/m^3$ for high terrain. To obtain such a variance requires both State and Federal approval.

SOURCE: Clean Air Act Amendments of 1977.

All other areas are designated as Class II, but states may redesignate these areas as Class I or III, provided certain requirements of Public Law 95-95 are fulfilled.

Similar air quality regulations may be applied to new facilities or significantly modified existing facilities in industrial areas where ambient air standards are being exceeded (nonattainment areas). Permits will be required for construction and operation of major new or modified sources and applicants will be required to achieve the "lowest achievable emission rate" (LAER) of any pollutant which exceeds the standards. This rate is defined as a rate of emissions which reflects:

- the most stringent emission limitation in the applicable state implementation plan unless the applicant can demonstrate that such limitations are not achievable; or
- the most stringent limitation which is actually achieved in practice by similar facilities.

Public Law 95-95 further requires that the permit to construct and operate may be issued only if:

- by the time the facility is to commence operation, total allowable emissions from all existing and new sources in the Air Quality Control Region, including the new or modified facility, will permit reasonable further progress toward attainment of the applicable national ambient air standard for the identified pollutant; or
- the emissions of such pollutant from the new or modified facility will not cause the total emissions of the pollutant to exceed the allowance permitted by the implementation plan for the pollutant from all new or modified sources in the area.

The purpose of these requirements is to allow, under strict stipulations, that the economic benefits to a region from introduction of new industry or new expansion of existing industry (new sources) may be obtained. The qualifying condition is that the new action must be accomplished in a way to assure progress toward compliance in the nonattainment area. Thus, permits issued by USEPA or the approved State agency must require "offsets" in the existing levels for pollutants which exceed Federal ambient air quality standards.

Offsets are enforceable reductions from the existing sources of air pollutants which will be greater than the emissions of those pollutants anticipated from the new source. A "new air quality benefit" must result from the combined new project plus the offsets attained (44 FR 3284, Part IV.A.4 and 44 FR 3275). The quantity of offsets must match the new source emissions on a "more than one-for-one" basis. The manner in which offsets may be attained is not specified. Several possible approaches have been used:

- when the new source is an expansion of an existing facility, the owner may install tighter controls on existing operations to achieve emissions which may be lower than those otherwise required for the existing sources;
- when the new source is an entirely new plant under a new owner in the nonattainment area, the applicant may reach an agreement with one or more existing sources whereby they agree to apply stricter pollution control measures, presumably in exchange for compensation by the new source applicant;
- in some instances, the applicant may purchase outright an existing facility, especially an obsolete facility with high pollutant emissions, and either clean it up or simply close it down;
- in cases where the state and/or local government are extremely interested in locating the new source industry in the area, say, due to the benefits to the local economy, they may assist the applicant either by putting pressure on the existing sources to achieve stricter pollution control standards or by public works actions such as paving of roads in the area to help reduce background particulate emissions.

The amount of time required to process PSD applications could run to several years in some controversial cases and adequate lead time for design, for modeling of air quality effects, and for required monitoring (one year) should be anticipated. The USEPA is committed to a policy of expediting permit application processing, public participation activities, and internal reviews so that the entire PSD review process could theoretically be carried out within 90 days after receipt of a complete and technically substantiated application. This time, however, could be extended by state review procedures, litigation, or offset arrangements in a highly industrialized nonattainment area. Hoffnagle and Dunlap (1978) emphasize that an industry should allow adequate time for the one-year baseline monitoring. Review and approval by regulatory agencies of the design of the monitoring plan at the earliest possible time can be a time saver. Total time involved in the PSD process for the permit applicant may realistically range from 18-43 months, as illustrated below (Hoffnagle and Dunlap 1978):

Activity	Time for Activity (Months)	Cumulative Time (Months)
Specify monitoring required	1-2	1-2
Select vendors and contractors	0-3	1-5
Procure and install equipment	1-4	2-9
Conduct 1-yr baseline monitoring	12	14-21
Complete data analysis, modeling and permit application	1-4	15-25
Request special model (if necessary) with agency hearing and review	0-6	15-31
Hearings on application and agency review	3-12	18-43

1.6.3 Solid Waste Regulations

The Resource Conservation and Recovery Act (RCRA), P.L. 94-580, defines "solid waste" as including solid, liquid, semisolid, or contained gaseous materials. Regulations implementing Subtitle C of the Act (40 CFR Part 261) provide that a solid waste is a hazardous waste if it is, or contains, a hazardous waste listed in Subpart D of Part 261 or the waste exhibits any of the characteristics defined in Subpart C. These charcateristics include:

- o Ignitability (flash point below 60° C (140° F)
- o Corrosivity
- o Reactivity
- o Toxicity

Hazardous wastes are identified in 40 CFR 261 Subpart D. The hazardous substances identified at this time in Subpart D do not include the major solid wastes of the phosphate fertilizer industry. However, this does not eliminate the possibility of industry wastes having "hazardous" designations in the future. Wastes containing arsenic or cadmium, for example, may be considered hazardous if the toxic materials can be leached out at concentrations of 5 mg/l and 1 mg/l, respectively, using the EP (Extraction Procedure) toxicity test. The natur of the wastes to be generated by a particular new source phosphate fertilizer plant will have to be carefully examined to determine the applicability of the hazardous waste designation.

All new facilities that will generate, transport, treat, store, or dispose of hazardous wastes must notify USEPA of this occurrence and obtain a USEPA identification number. Storage, treating, and disposal also require a permit.

The determination of whether wastes generated or handled are hazardous is the responsibility of the owner or operator of the generating or handling facility. The first step is to consult the promulgated list (CFR 261 Subpart D). If the waste is not listed, the second step is to determine whether the waste exhibits any of the hazardous characteristics of listed through analytical tests using procedures promulgated in the regulations of by applying known information about characteristics of the waste based on process or materials used.

If it is determined that a hazardous waste is generated, it should be quantified to determine applicability of the small generator exemption. This cutoff point is 2,200 pounds per month, but it drops to 2.2 pounds for any commercial product or manufacturing chemical intermediate having a generic name listed in Section 261.33. Containers that have been used to contain less than 21 quarts of Section 261.33 materials and less than 22 pounds of liners from such containers are also exempt. It is anticipated that this exemption may be available to many very small plants with, for example, only one machine tool and one small painting operation. However, as more information is obtained on the behavior of substances in a disposal environment, the terms of this exemption may be altered from time to time.

The hazardous waste management system is based on the use of a manifest prepared by the generator describing and quantifying the waste and designating a disposal, treatment, or storage facility permitted to receive the type waste described to which the waste is to be delivered. One alternate site may be designated. Copies of the manifest are turned over to the transporter and a copy must be signed and returned to the generator each time the waste changes hands. If the generator does not receive a copy from the designated receiving facility or alternate within 35 days, he must track the fate of the waste through the transporter and designated facility or facilities. If the manifest copy is not received in 45 days, the generator must file an Exception Report with USEPA or the cognizant state agency.

A copy of each manifest must be kept for three years or until a signed copy is received from the designated receiving facility. In turn, the signed copy must be kept for three years. The same retention period applies to each Annual Report required whether disposal, storage, or treatment occurs on-site or off-site.

The generator must also:

- package the waste in accordance with the applicable DOT regulations under 49 CFR Parts 173, 178, and 179;
- label each package in accordance with DOT regulations under 49 CFR 172;
- mark each package in accordance with the applicable DOT regulations under 49 CFR 172;
- mark each container of 110 gallons or less with the following DOT (49 CFR 172) notice:

  > "Hazardous Waste - Federal Law Prohibits Improper Disposal. If found, contact the nearest police or public safety authority or the U.S. Environmental Protection Agency."

- supply appropriate placards for the transporting vehicle in accordance with DOT regulations under 49 CFR Part 172, Subpart F.

Waste in properly labelled and dated containers in compliance with the regulations may be stored on the generator's premises for up to 90 days without a storage permit. This is to permit time for accumulation for more economic pickup or to find an available permitted disposal facility.

Due to the cost and stringent design and operating requirements for permitted landfills, it is anticipated that most new generator plants will utilize off-site disposal facilities. However, any companies desiring to construct their own will be subject to 40 CFR Part 264.

Incineration is considered to be "treatment," and, as such, is also subject to Part 264 as are chemical, physical, and biological treatment of hazardous wastes, and a permit will be required. Totally enclosed treatment systems--such as in-pipe treatment of acid and alkaline solutions--are not subject to this part.

Although underground injection of wastes constitutes "disposal" as defined by RCRA, this activity will be regulated by the underground injection control (UIC) program adopted pursuant to the Safe Drinking Water Act (P.L. 93-523). The consolidated permit regulations (40 CFR Parts 122, 123, 124) govern the procedural aspects of this program; the technical considerations are contained in 40 CFR Part 146.

The disposal of innocuous solid wastes is subject to Subtitle D of RCRA and the implementing regulations (40 CFR Part 256). Recovery or disposal in an approved sanitary landfill will be required under a state program. Disposal in open dumps is prohibited. All existing state regulations which do not meet the requirements of Subtitle D are superseded.

1.6.4 Monitoring Requirements

In addition to applying the best available technology to abate and control adverse environmental impacts from air emissions, wastewater streams, and land disposal of wastes, an NPDES permit applicant will be required to demonstrate compliance with applicable pollution control regulations. The NPDES permit itself may require monitoring, recording, and recordkeeping on flow of all pollutants that are subject to reduction or elimination under the terms and conditions of the permit, as well as any other pollutant as required by the State or USEPA. Monitoring intervals must be sufficiently frequent to yield data that reasonably characterize the nature of the discharge.

Similarly, monitoring of leachate, runoff, and air emissions will be required under the Federal RCRA on sites where wastes determined to be hazardous are landfilled. In addition, it is not inconceivable that some type of monitoring may be required for some, if not all, disposal sites for non-hazardous wastes to ensure that "there is no reasonable probability of adverse effects on health of the environment" (Section 4004(a), RCRA).

2.0 IMPACT IDENTIFICATION

2.1 PROCESS WASTES

2.1.1 Materials Balance and Typical Waste Characteristics

2.1.1.1 Sulfuric Acid Production

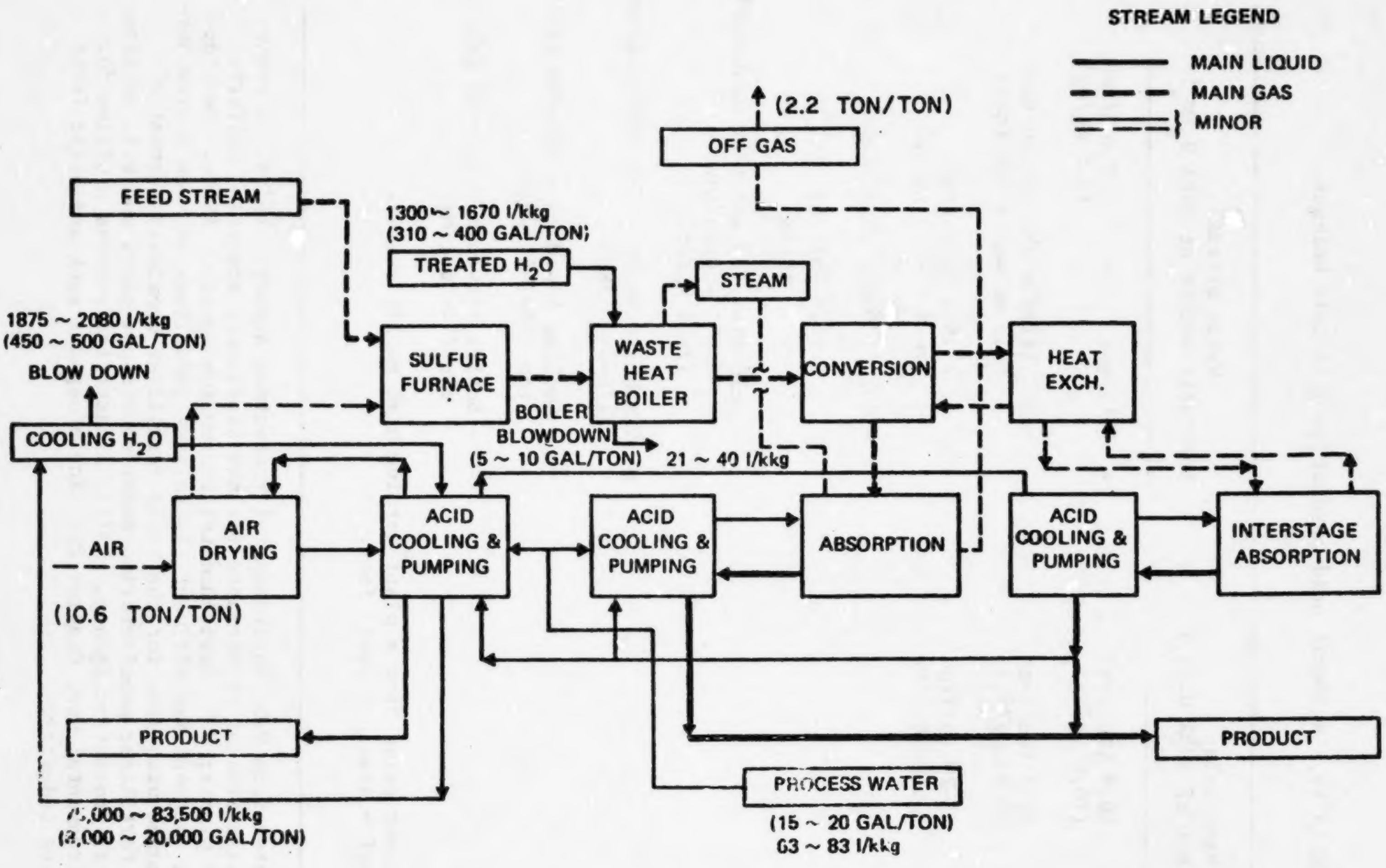
The only wastewater streams produced in the sulfuric acid production process are blowdown from boilers and cooling towers. Figure 33 illustrates the blowdown sources and quantities for a typical installation using double absorption; older units using single absorption produce the same wastewater quantities. A materials balance for sulfuric acid production is given in Table 19.

A plant producing phosphoric acid will usually include sulfuric acid production. The EID should include the operating data categories listed above. Several plants built since 1971 have installed single absorption process designs, usually with an ammonia scrubbing type of emission control system for SO_2 removal, but double absorption is preferred by most operators, depending on economic variables (Section 3.2.1).

Cooling Water Contaminants

The EID should include computations of planned quantities of cooling water blowdown and list the probable range of contaminants, based on operating parameters and make-up water quality. The quality of cooling system blowdown varies both with the level of impurities in the make-up water and the amount and types of inhibitor chemicals used. Data collected for the effluent guidelines study (USEPA 1974a) indicated the following normal range of contaminants in cooling water blowdown:

Contaminant	Concentration (mg/l)
Chromate	0-250
Sulfate	500-3000
Chloride	35-160
Phosphate	10-50
Zinc	0-30
TDS	500-10,000
SS	0-50
Biocides	0-100


STREAM LEGEND
MAIN LIQUID
MAIN GAS
MINOR
(2.2 TON/TON)
OFF GAS
FEED STREAM
1300 ~ 1670 l/kkg
(310 ~ 400 GAL/TON)
TREATED H2O
STEAM
1875 ~ 2080 l/kkg
(450 ~ 500 GAL/TON)
BLOW DOWN
SULFUR FURNACE
WASTE HEAT BOILER
CONVERSION
HEAT EXCH.
BOILER BLOWDOWN
(5 ~ 10 GAL/TON) 21 ~ 40 l/kkg
COOLING H2O
AIR
AIR DRYING
(10.6 TON/TON)
ACID COOLING & PUMPING
ACID COOLING & PUMPING
ABSORPTION
ACID COOLING & PUMPING
INTERSTAGE ABSORPTION
PRODUCT
PRODUCT
PROCESS WATER
(15 ~ 20 GAL/TON)
63 ~ 83 l/kkg
75,000 ~ 83,500 l/kkg
(8,000 ~ 20,000 GAL/TON)

TON = SHORT TON
kkg = METRIC TON

Figure 33. Sulfuric acid plant - double catalysis (flow rates per ton 100% H_2SO_4).

Source: Adapted from U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC, 168 p.

Table 19. Sulfuric acid production materials balance.

Input Materials (per unit weight of 100% H_2SO_4)	Waste Streams (per unit weight of 100% H_2SO_4)
• Air - 10.6 ton/ton (10.6 Mg/Mg)	• Tail gas - 2.2 ton/ton (2.2 Mg/Mg)
• Sulfur - 0.33 ton/ton (0.33 Mg/Mg)	- SO_2 (single absorption with no emission controls) 21.5 - 85 lb/ton (10.8 - 42.5 kg/Mg)
• Water - 15-20 gal/ton (3.6-4.8 l/Mg)	- SO_2 (double absorption) (1.8 lb/ton) (0.9 kg/Mg)
	- Acid mist (no emission controls) 0.4[a] - 9 lb/ton (2-50 mg/scf)[b]
	• Discharge water - 710-1000 gal/ton (170-240 l/Mg)
	- Cooling blowdown - 400-600 gal/ton (96-144 l/Mg)
	- Boiler blowdown - 310-400 gal/ton (74-96 l/Mg)

Notes: a. Lower value from a plant burning high purity sulfur.
b. scf = standard cubic foot.

SOURCE: Adapted from U.S. Environmental Protection Agency. 1978a. A review of standards of performance for new stationary sources - sulfuric acid plants; U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category; and U.S. Environmental Protection Agency. 1977b. Industrial process profiles for environmental use, Chapter 22: The phosphate rock and basic fertilizers industry.

The EID should describe the proposed method of treating cooling tower blowdown. It can be treated separately or combined with other plant effluents for treatment. The method to be employed depends on the chemical treatment method used and other cost factors. Those plants which utilize chromate or zinc treatment compounds generally treat the blowdown stream separately to minimize effluent treatment costs (USEPA 1974a).

Boiler Blowdown Contaminants

The EID should report anticipated quantities and contaminant levels for boiler blowdown. The typical range of contaminant concentrations reported in the effluent guidelines study (USEPA 1974a) for 310-400 gal/ton of boiler blowdown are listed below:

Contaminant	Concentration (mg/1)
Phosphate	5-50
Sulfite	0-100
TDS	500-3,500
Zinc	0-10
Alkalinity	50-700
Hardness	50-500
Silica (SiO_2)	25-80

To date, no effluent guidelines for either thermal discharge or contaminants associated with boiler blowdown have been proposed or promulgated, but contaminants are monitored and State and/or USEPA regional offices involved in new source permitting set up contaminant criteria. The EID should demonstrate that boiler blowdown contaminants levels will conform to the locally applicable criteria.

Air Emissions

Recent test data are available illustrating compliance with SO_2 and acid mist emissions. The study done by the MITRE Corporation for USEPA to evlaute sulfuric acid plant NSPS (USEPA 1978a) obtained 29 sets of data representing all 32 new sulfuric acid units built since the NSPS were issued. The results indicate tested emission levels which can be compared with EID projections for SO_2 and acid mist emissions (Table 20). Figures 34 and 35 display the data

Table 20. New source performance standards compliance test results for sulfuric acid plants

EPA Region	Company	Plant Location	Nominal Unit Size (100% H_2SO_4) Mg/day/TPD	Average SO_2 Emissions kg/Mg of 100% H_2SO_4 (lb/ton)	Average Acid Mist Emissions kg/Mg of 100% H_2SO_4 (lb/ton)	Actual Plant Product Rate During NSPS Test Mg/day 100% H_2SO_4 (TPD)	Measured Opacity During Test (Percent)	Reference
II	NL Industries, Inc.	Sayreville, N.J.	910 (1000)	0.71 (1.42)	0.018 (.035)	845 (929)	0	Mistry et al., 1975
			910 (1000)	1.9 (3.7)	0.062 (.123)	808 (888)	0	Mistry et al., 1975
IV	Agrico Chemical, Inc.	So. Pierce, Fla.	1640 (1800)	1.11 (2.22)	0.055 (0.109)	1629 (1790)		CDS, 1978
	CF Chemicals, Inc.	Bartow, Fla.	1800 (2000)	0.56 (1.12)	0.010 (0.021)	1781 (1957)		CDS, 1978
	CF Chemicals, Inc.	Plant City, Fla.	1460 (1600)	0.76 (1.52)	0.058 (0.116)	1562 (1717)		CDS, 1978
			1460 (1600)	1.26 (2.52)	0.026 (0.052)	1277 (1403)		CDS, 1978
	Gardinier, Inc.	Tampa, Fla.	2370 (2600)	0.97 (1.94)	0.036 (0.071)	2424 (2664)	0±5	Garrett, 1978
			1460 (1600)	0.87 (1.73)	0.030 (0.061)	1616 (1776)	0±5	Garrett, 1978
	W.R. Grace Co.	Bartow, Fla.	1460 (1600)	0.16 (0.32)	0.03 (0.06)	1547 (1700)		CDS, 1978
			1460 (1600)	1.03 (2.16)	0.02 (.04)	1535 (1687)		Wu, 1978
			1460 (1600)	1.2 (2.3)	0.07 (0.13)	1643 (1805)		Wu, 1978
	IMC Chemical Corp.	Mulberry, Fla.	1800 (2000)	0.73 (1.45)	0.008 (0.016)	2457 (2700)		CDS, 1978
			1800 (2000)	0.79 (1.58)	0.008 (0.016)	2366 (2600)		CDS, 1978
			1800 (2000)	0.65 (1.30)	0.011 (0.022)	2503 (2750)		CDS, 1978
	Occidental Petroleum Corp.	White Springs, Fla.	1640 (1800)	1.62 (3.23)	0.071 (0.142)	1756 (1930)		CDS, 1978
			1640 (1800)	0.47 (0.93)	0.064 (0.127)	1641 (1803)		CDS, 1978
	Am. Cyanamid Co.	Savannah, Ga.	730 (800)	1.17 (2.33)	0.030 (0.059)	779 (856)		Gardner, 1978
	Mississippi Chemical Corp.	Pascagoula, Miss.	1370 (1500)	0.48 (0.95)	0.064 (0.128)	1387 (1524)		CDS, 1978
	Texasgulf, Inc.	Lee Creek, N.C.	1370 (1500)	0.85 (1.70)	0.023 (0.046)	1474 (1620)		CDS, 1978
			1370 (1500)	0.91 (1.82)	0.037 (0.073)	1313 (1443)		CDS, 1978
V	Amlin Corp.[a]	Wood River, Ill.	230 (250)	1.85 (3.69)	0.072 (0.144)	219 (241)		Cohen, 1978
VI	Agrico Chemical, Inc.	Donaldsonville, La.	1640 (1800)	0.55 (1.10)	0.037 (.073)	1830 (2011)	<10	Shook, 1978
	Agrico Chemical, Inc.		1640 (1800)	0.55 (1.11)	0.042 (0.085)	1677 (1843)	<10	Shook, 1978
	Freeport Chemical Co.	Convent, La.	1460 (1600)	1.0 (1.99)	0.08 (0.15)	1694 (1862)		Spruiell, 1978
	Rohm & Haas, Inc.	Deer Park, Tx.	640 (700)	1.16 (2.32)	0.041 (0.082)	716 (787)	9.2	Spruiell, 1978
IX	Valley Nitrogen Producers, Inc.	Helms, Calif.	1640 (1800)	0.40 (0.79)	0.04 (.07)		<5	Reynolds, 1978
X	Beker Industries, Inc.	Conda, Idaho	770 (850)	1.56 (3.02)	0.053 (0.105)	1001 (1100)		Pfander, 1978
	J.R. Simplot Co.	Pocatello, Idaho	810 (900)[b]	0.53 (1.05)[b]	0.046 (0.092)[b]	853 (938)[b]		Pfander, 1978
	Allied Chemical Corp.	Anacortes, Wash.	300 (330)	1.70 (3.41)[c]	0.04 (0.07)[c]	222 (244)	5	Sowden & Algeard, 1976

---

[a] This facility was purchased by Shell Oil Co. in 1976; the plant is being modified to incorporate a double absorption process for SO_2 control.

[b] Total output of two units.

[c] Average of three units.

Source: U.S. Environmental Protection Agency. 1978a. A review of standards of performance for new stationary sources - sulfuric acid plants. Prepared by Marvin Drabkin and Kathryn J. Brooks, MITRE Corp., McLean VA. Variously paged, 80 p.

graphically and indicate a high degree of scatter. This scatter has been interpreted to indicate problems in the USEPA Method 8 used since 1971 to monitor compliance. If so, the probable effect has been that some SO_2 results are low and some acid mist results are high. Method 8 was revised effective August 18, 1977 (USEPA 1978a).

2.1.1.2 Phosphate Rock Processing

The EID should include operating data for rock processing, which includes handling, grinding, and storage of the beneficiated phosphate rock. Table 21 indicates the materials balance for phosphate rock processing.

Table 21. Phosphate rock processing materials balance.

Input Materials (per unit weight of marketable rock)	Waste Streams (per unit weight of marketable rock)
• Phosphate rock - 1 ton/ton (1 Mg/Mg)	• Particulates - less than 20 lb/ton (10 kg/Mg)
• Cooling water - 8-150 gal/ton (33-625 l/Mg)	• Cooling water - 8-150 gal/ton* (33-625 l/Mg)

*non-contaminated - temperature increase only in discharge.

SOURCE: U.S. Environmental Protection Agency. 1974a. Development document limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category; and U.S. Environmental Protection Agency. 1977b. Industrial process profiles for environmental use, Chapter 22: The phosphate rock and basic fertilizers industry.

The option to utilize wet grinding does not substantially alter the information in Table 21. The small amount of make-up water introduced in the grinding operation is transferred to the next process and is equivalent to a slight lowering of the sulfuric acid concentration in the acidualtion operation. Definitive data on quantities of particulate air emissions generated are not available.

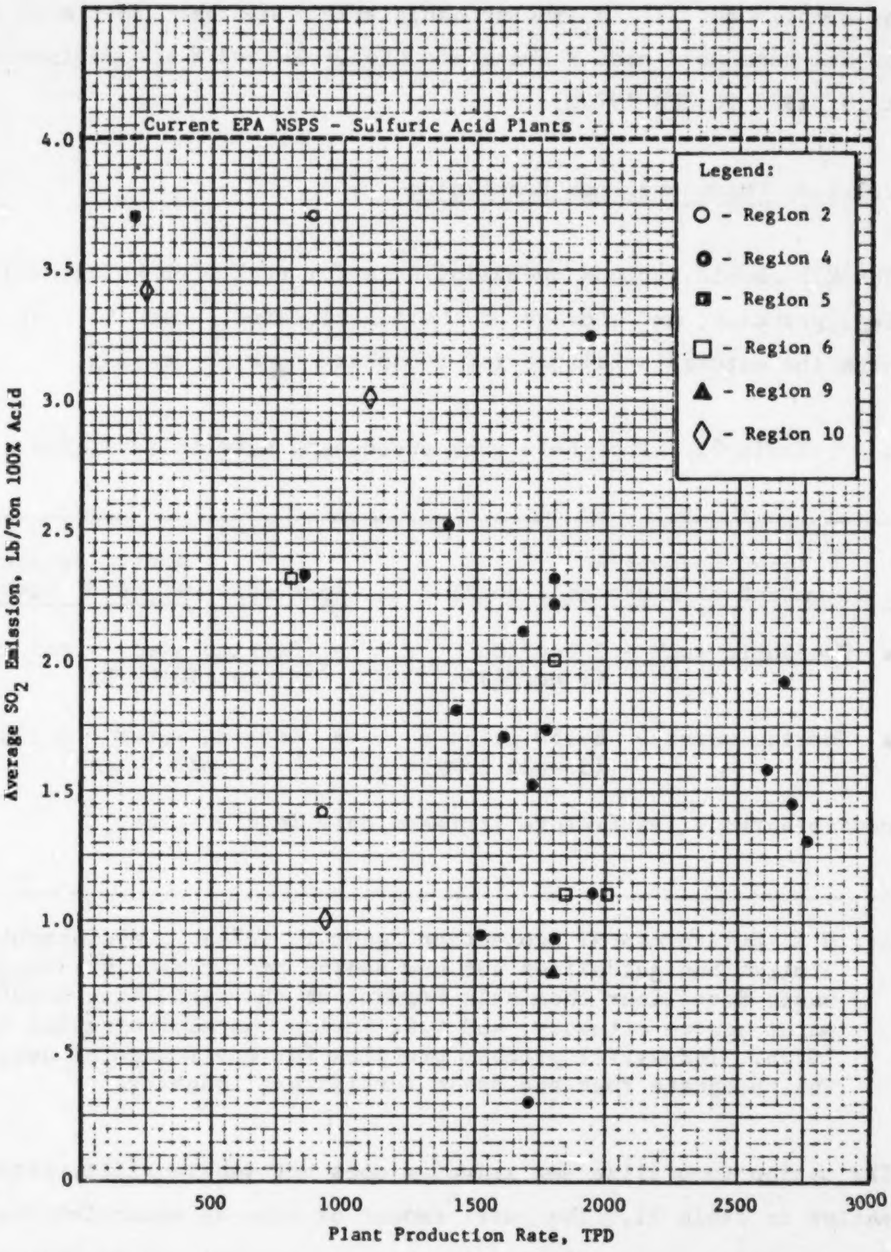


Figure 34. Contact process sulfuric acid plants, SO_2 emissions.

Source: U.S. Environmental Protection Agency. 1978a. A review of standards of performance for new stationary sources - sulfuric acid plants. Prepared by Marvin Drabkin and Kathryn J. Brooks, MITRE Corporation, McLean VA. Variously paged.

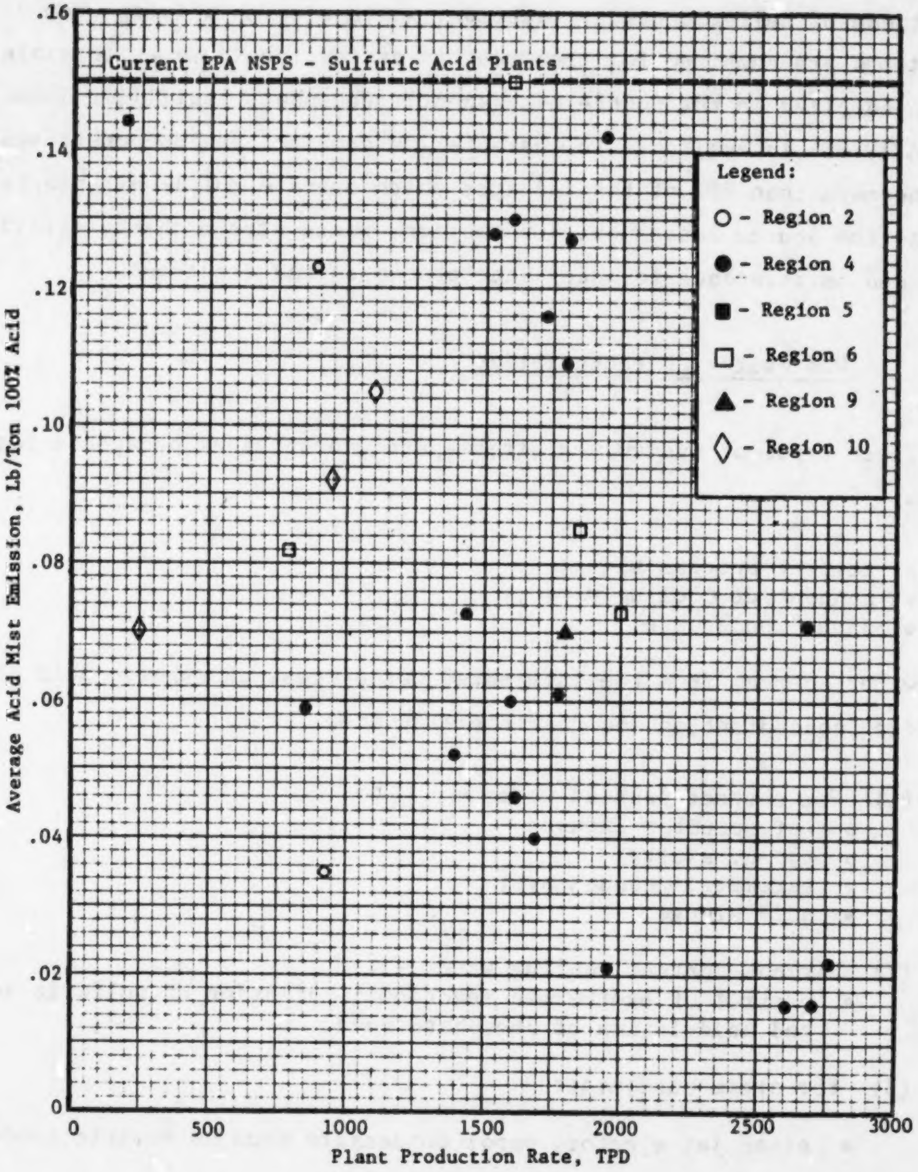


Figure 35. Contact process sulfuric acid plants, acid mist emissions.

Source: U.S. Environmental Protection Agency. 1978a. A review of standards of performance for new stationary sources - sulfuric acid plants. Prepared by Marvin Drabkin and Kathryn J. Brooks. MITRE Corporation, McLean VA. Variously paged, 80 p.

2.1.1.3 Wet Process Phosphoric Acid Production, Concentration, and Clarification

Because of the integrated nature of the phosphate fertilizer processes downstream of sulfuric acid production, waste streams arising from different operations are combined for treatment at as few locations as feasible. Information compiled in the Source Assessment: Phosphate Fertilizer Industry (USEPA 1979a) is available to characterize combined and component waste streams for the more than 80% of the industry which operate multi-unit plants. To utilize the Source Assessment information, waste stream characteristics are discussed in reference to integrated processes and treatment.

Wastewater Characteristics

Three types of wastewater streams are generated at phosphate fertilizer plants:

- contact process water;
- noncontact cooling water;
- steam condensate.

Wastewater sources from the integrated wet process phosphoric acid production including concentration and clarification are:

(1) For contact process water -
  - wet scrubber liquor;
  - gypsum slurry;
  - barometric condensers;
  - acid sludge.

(2) For non-contact cooling water -
  - control of exothermic reaction in dilution of sulfuric acid and acidulation of phosphate rock.

(3) For steam condensate -
  - steam jet ejector, vapor condensate from barometric condenser.

Wet Process Phosphoric Acid Processes

The EID should include operating data to support projected waste stream rates. Table 22 is a materials balance including typical values from the USEPA Development Document (USEPA 1974a). Figures 36 and 37 illustrate input and outflow quantities of materials in the production of wet process phosphoric acid and superphosphoric acid.

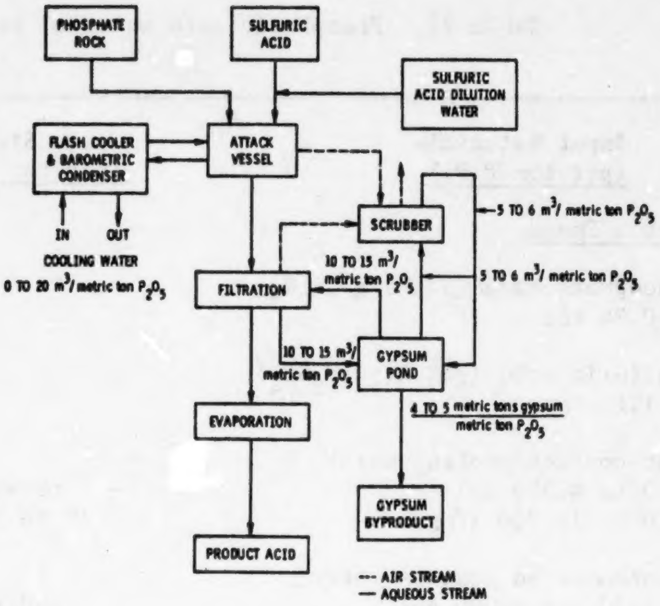

PHOSPHATE ROCK
SULFURIC ACID
SULFURIC ACID DILUTION WATER
FLASH COOLER & BAROMETRIC CONDENSER
ATTACK VESSEL
IN
OUT
COOLING WATER
0 TO 20 m^3/metric ton P_2O_5
SCRUBBER
5 TO 6 m^3/ metric ton P_2O_5
10 TO 15 m^3/ metric ton P_2O_5
FILTRATION
5 TO 6 m^3/ metric ton P_2O_5
10 TO 15 m^3/ metric ton P_2O_5
GYPSUM POND
4 TO 5 metric tons gypsum / metric ton P_2O_5
EVAPORATION
GYPSUM BYPRODUCT
PRODUCT ACID
--- AIR STREAM
— AQUEOUS STREAM

Figure 36. Wet process for production of phosphoric acid.

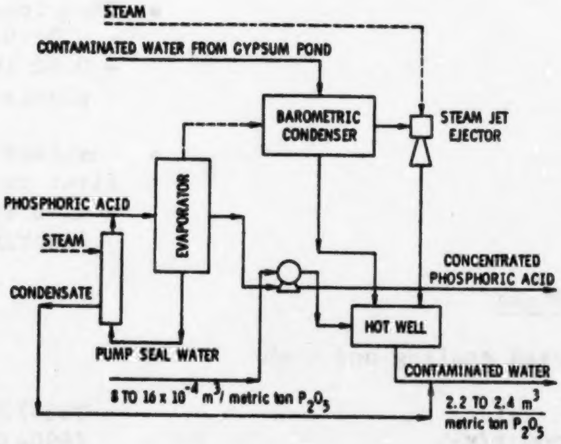

STEAM
CONTAMINATED WATER FROM GYPSUM POND
BAROMETRIC CONDENSER
STEAM JET EJECTOR
PHOSPHORIC ACID
EVAPORATOR
STEAM
CONDENSATE
CONCENTRATED PHOSPHORIC ACID
HOT WELL
PUMP SEAL WATER
CONTAMINATED WATER
8 TO 16 x 10^{-4} m^3/ metric ton P_2O_5
2.2 TO 2.4 m^3 / metric ton P_2O_5

Figure 37. Production of superphosphoric acid.

Source (Figures 36 and 37): U.S. Environmental Protection Agency. 1977a. (Preliminary) Source assessment: Phosphate fertilizer industry, phosphoric acid and superphosphoric acid. Office of Research and Development. Washington DC. Prepared by G.D. Rawlings, E.A. Mullen, and J.M. Nyers, Monsanto Corporation, Dayton OH, 93 p.

Table 22. Phosphoric acid material balance.

Input Materials (per ton P_2O_5)	Waste Streams (per ton P_2O_5)
Acidulation Phase	
• Phosphate rock (32% avg. P_2O_5) - 0.96 ton	
• Sulfuric acid (93% avg. H_2SO_4) - 1.11 ton	
• Non-contact cooling water - 0 to 4,500 gal (0 to 19,000 l/Mg)	- 0 to 4,500 gal (0 to 19,000 l/Mg)
• Contaminated process water - 3,800 to 5,000 gal (16,400 to 20,800 l/Mg)	- 3,800 to 5,000 gal (16,400 to 20,800 l/Mg)
Concentration Phase	
• Contaminated process water - 550-570 gal (2500-2600 l/Mg)	- 550-570 gal (+0.2-0.4 gal) condensate) (2500-2600 l/Mg)
	• Fluorides emissions - 0.02-0.07 lb - 0.60 lb in poorly controlled plants
	• Combined gypsum wastes from first two phases - 1.36 tons (contains 0.5% fluorine)
Clarification Phase	
• Contaminated cooling and wash water - 165-770 gal (690-3200 l/Mg)	- 165-770 gal (690-3200 l/Mg)

Table 22. Phosphoric acid (concluded).

Input Materials (per ton P_2O_5)	Waste Streams (per ton P_2O_5)
Superphosphoric Acid Phase	
• Input quantities not available	• Fluorides - less than 0.01 lb. for vacuum evaporation process - 0.12 lb for submerged combustion process

SOURCES: U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category; U.S. Environmental Protection Agency. 1977a. (Preliminary) Source assessment: Phosphate fertilizer industry, phosphoric acid and superphosphoric acid, Office of Research and Development, Washington DC, U.S. Environmental Protection Agency. 1974b. Background information for standards of performance: Phosphate fertilizer industry, Volume 1, Proposed standards; U.S. Environmental Protection Agency. 1977c. Final guideline document: Control of fluoride emissions from existing phosphate fertilizer plants.

2.1.1.4 Dry Phosphate Fertilizer Production

Plants which produce NSP, TSP, and ammonium phosphates have similar waste stream characteristics. The wet scrubber liquor is the only process wastewater stream generated. Recycled gypsum pond water is used in the scrubber system to reduce the level of fluoride gases and particulate matter evolved from the mixer, den, and conveyors at NSP and run of pile TSP plants. At granular TSP plants, offgases from the reactor, mixer, dryer, granulator, cooler, and screens are absorbed in the scrubbing water. At ammonium phosphate plants, wet scrubbers are used primarily for ammonia recovery from the acid neutralizer and ammoniator-granulator. Weak (28% P_2O_5) phosphoric acid is used as the scrubbing liquor and is recycled back to the ammoniator-granulator. Secondary wet scrubber systems are occasionally used to further remove fluorides, particulates, ammonia, and combustion products issuing from the dryer, cooler, and product screening operations. This secondary system uses contaminated water as a scrubber liquor and is therefore a wastewater source (USEPA 1979a).

The wastewater and air emissions produced in the three solid product processes are similar, with the addition of ammonia to wastewaters in ammonium phosphates production. Since the processes all yield a salable end product and do not feed into one another, three separate materials balances are given in Tables 23, 24,, and 25.

Quantifying data for MAP and DAP ammonium phosphate processes are not available for feedstocks. Wastewater streams associated with these conventional processes, estimated in the USEPA Development Document, are given below:

	Contaminated Water - Input	Waste Stream
MAP	- 1200-1500 gal/ton (5000-6500 l/Mg)	- 0-72 gal/ton[*] (0-300 l/Mg)
DAP	- 1200-1500 gal/ton (5000-6500 l/Mg)	- 1200-1500 gal/ton (5000-6500 l/Mg)

[*] The fate of the difference in input and waste stream water is not accounted for.

Table 23. Normal superphosphate materials balance.

Input Materials (per ton of NSP)	Waste Streams (per ton of NSP)
● Phosphate rock (34% avg. P_2O_5) - 1200 to 1220 lb (600 to 610 kg/Mg)	
● Sulfuric acid (100% H_2SO_4 basis) - 700 to 720 lb (350 to 360 kg/Mg)	● Fluorine (solid waste or byproduct) - 16 to 20 lb (as CaF, from removal in limestone beds) (8 to 10 kg/Mg)
● Contaminated water (scrubbers) - 225 to 250 gal (940 to 1040 l/Mg)	- 225 to 250 gal (940 to 1040 l/Mg)

SOURCES: U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category; U.S. Environmental Protection Agency. 1977b. Industrial process profiles for environmental use, Chapter 22: The phosphate rock and basic fertilizers industry. Office of Research and Development, Cincinnati OH.

Table 24. Granular triple superphosphate materials balance.

Input Materials (per ton of GTSP)	Waste streams (per ton of GTSP)
• Phosphate rock (34% avg. P_2O_5) - 840 to 880 lb (420 to 440 kg/Mg)	
• Phosphoric acid (53% avg. P_2O_5) - 980 to 1020 lb (490 to 510 kg/Mg)	• Fluorine (solid waste or byproduct) - 20 to 24 lb (as CaF, from removal in limestone beds) (10 to 12 kg/Mg) - emissions of 0.20 to 0.60 lb are reported (0.10 to 0.30 kg/Mg)
• Contaminated water (scrubbers)	
- 158-180 gal (660-750 l/Mg)	- 5-10 gal (21-40 l/Mg)

SOURCES: U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category; U.S. Environmental Protection Agency. 1977b. Industrial process profiles for environmental use, Chapter 22: The phosphate rock and basic fertilizers industry. Office of Research and Development, Cincinnati OH.

Table 25. Ammonium phosphate materials balance (12-48-0-3.6S, MAP sulfate, 3-inch pipe-cross reactor with ammoniator-granulator.

Input Materials (per ton of product)	Waste Streams (per ton of product)
● Ammonia	
- 293 lb (147 kg/Mg)	- 2-3 lb (recoverable in scrubbers) (1.0-1.5 kg/Mg)
● Sulfuric acid (93% H_2SO_4)	
- 228 lb (144 kg/Mg)	
● Phosphoric acid (54% P_2O_5)	
- 1865 lb (932 kg/Mg)	
● Make-up water	
- 59 lb (30 kg/Mg)	
● Contaminated water (scrubbers)	
- 1200-1430 gal* (5000 - 6000 l/Mg)	- 1200-1430 gal* (5000 - 6000 l/Mg)

*Surmised, based on DAP scrubber requirements (USEPA 1979a); quantities may be less with pipe-cross reactor.

SOURCES: Compiled from Parker, B.R., M.M. Norton, and D.G. Salladay. 1977. Developments in production of granular NP and NPK fertilizers using the pipe and pipe-cross reactor; U.S. Environmental Protection Agency. 1979a. Source assessment: Phosphate fertilizer industry. Office of Research and Development, Washington DC.

2.1.1.5 Gypsum Pond Characteristics

The EID should detail the design and capacity of wastewater storage arrangements. All contaminated wastewater in new source phosphate fertilizer facilities will be retained in gypsum ponds or recirculated using cooling towers. Use of cooling towers is possible but usually economically impractical. Furthermore, meeting the no-discharge requirement becomes extremely difficult without the freeboard buffer of the gypsum pond and precise water balance among processes. More than 90% of the wet process phosphoric acid plants in the United States use gypsum ponds (TRC 1979).

Besides being a reservoir and cooling pond, the gypsum pond plays an integral part in the wastewater treatment scheme. The pond serves as a settling basin for gypsum and other waste solids. To function properly and avoid effluent discharge to surface waters, the size of the gypsum pond at a wet process phosphoric acid plant is approximately 2.23×10^{-3} km^2/metric ton P_2O_5/day. Gypsum ponds are located adjacent to the plant complex; they are, in many cases, abandoned phosphate rock mine pits (USEPA 1979a).

In most plants, more than one wastewater containment area is available. As one gypsum pond becomes filled, the gypsum slurry is diverted to another area and the original pond is dried and excavated into piles (TRC 1979). In large ponds used for both cooling and gypsum settling, the area where gypsum slurry enters the pond, where most of the gypsum settles, is known as the gypsum flats. Wet gypsum from this area of the pond is removed by draglines and transferred to an active gypsum pile while clarified gypsum pond water farther downstream continues to be recycled to the plant (USEPA 1978c). With each recycle, the level of dissolved contaminants in the water increases. After 3 to 5 years of recycle, impurities in the pond waters approach equilibrium concentrations (USEPA 1978c), a function of pH and temperature, which is maintained by volatilization and precipitation of impurities (USEPA 1979a). The typical ranges of equilibrium concentrations are shown in Table 26 (USEPA 1978c).

Table 26. Typical equilibrium composition of gypsum pond water.

Contaminant	Concentration, g/m^3
Phosphorus pentoxide, equivalent	6,000 to 12,000
Fluoride	3,000 to 5,000
Sulfate	2,000 to 4,000
Calcium	350 to 1,200
Ammonia	0 to 100
Nitrate	0 to 100
Silica	1,600
Aluminum	100 to 500
Iron	70 to 300
pH	1.0 to 1.8

SOURCES: U.S. Environmental Protection Agency. 1978c. Evaluation of emissions and control techniques for reducing fluoride emissions from gypsum ponds in the phosphoric acid industry in U.S. Environmental Protection Agency. 1979a. Source assessment: Phosphate fertilizer industry. Office of Research and Development, Washington DC.

At pH less than 2, it is estimated that 80% of the phosphate present exists as H_3PO_4, the remaining 20% being the anion H_2PO_4 (USEPA 1978c). The major equilibrium of fluoride compounds as depicted in a model developed by Environmental Science and Engineering, Inc., is shown in Figure 38 (USEPA 1978c). In addition to the predominant compounds fluosilicic acid (H_2SiF_6) and hydrogen fluoride (HF), small amounts of fluoride will be present in the water as soluble and insoluble aluminum and iron complexes. In addition, concentrations of radium-226 in gypsum pond water reach 60-100 picocuries/liter (USEPA 1974a).

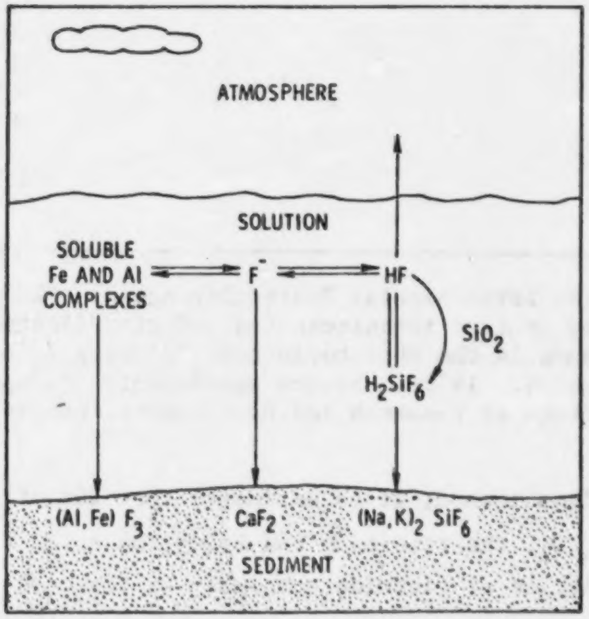

ATMOSPHERE
SOLUTION
SOLUBLE Fe AND Al COMPLEXES
F^-
HF
SiO_2
H_2SiF_6
$(Al,Fe)F_3$
CaF_2
$(Na,K)_2SiF_6$
SEDIMENT

Figure 38. Major gypsum pond equilibrium.

Source: U.S. Environmental Protection Agency. 1978c. Evaluation of emissions and control techniques for reducing fluoride emissions from gypsum ponds in the phosphoric acid industry. Research Triangle Park NC, 218 p. in USEPA 1979a.

2.1.1.6 Solid Waste Characteristics

There are three sources of solid residue in the phosphate fertilizer industry (USEPA 1979a):

- gypsum from the filtration of wet process phosphoric acid
- wet process phosphoric acid sludge
- wet scrubber liquor

The quantity of gypsum produced in a wet process phosphoric acid plant ranges from 4.6 to 5.2 metric tons of gypsum/metric ton P_2O_5 produced. As a rule of thumb, approximately 1,360 m^3 of gypsum will be accumulated yearly per metric ton of P_2O_5 produced per day (Slack 1968).

A second source of solid residue is the phosphate rock from which impurity-bearing minerals settle out of the clarifier to form acid sludges. Phosphate rock salts which contribute to the formation of acid sludges include: fluorine, iron, aluminum, silicon, sodium, and potassium salts. Table 27 shows an analysis of solids collected at various stages of wet process phosphoric acid production.

Table 27. Analysis of solids from wet process phosphoric acid.

	Analysis						
Solids from	Phosphorus pentoxide	Calcium	Sulfate	Aluminum	Iron	Fluorine	Silica
32% P_2O_5 acid (feed to evaporators)	1.9	14.8	38.9	0.3	0.2	19.9	10.3
54% P_2O_5 acid from evaporators	6.8	12.9	29.0	5.1	0.3	22.0	5.3
54% P_2O_5 acid after storage	38.9	3.3	4.7	1.5	9.6	12.9	6.1

Reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc. Year of first publication 1968.

Fluosilicates, fluorides, silica, cryolite (Na or K)$_3AlF_6$), sulfates, unreacted phosphate rock, and various other combinations of the impurities as complex salts have been identified in the acid sludge. The separated solids can either be dried and sold as fertilizer or sent to the gypsum pond. Effluent from the clarification process ranges from 0.7 m^3 to 3.2 m^3/metric ton P_2O_5 (USEPA 1974a).

The third source of solid residue wastes is the wet scrubber liquor. At ammonium phosphate plants, for example, the scrubber liquor going to the gypsum pond contains about 10 g of solid residue/kg P_2O_5. This solid residue is primarily hydrated silicon oxides ($SiO_2 \cdot xH_2O$). Solid residue values for wet scrubber systems at the other phosphate fertilizer operations are not available, but they should be similar to those for ammonium phosphate plants (USEPA 1979a).

Approximately 99% of the solid residue wastes are stored at phosphate fertilizer plants. The remaining 1% is sold as a raw material for various products. Radioactivity of solid wastes varies depending on process and type of waste. For example, phosphate rock product contains about 42 picocuries per gram (pCi/g) radium-226, whereas by-product gypsum from acid plants contains 21-33 pCi/g. Due to the relative solubility of gypsum, however, seepage water from gypsum piles can be as high as 90-100 pCi/l. An Office of Radiation Programs study has recommended that moisture control techniques be considered in land disposal of gypsum pile wastes (USEPA 1977d), but this is not current practice.

Rainfall drainage from the gypsum piles is collected in a ditch and recycled to the gypsum pond. A major concern regarding these wastes is the large amount of land area required to store the gypsum and the unsightly appearance of the piles of gypsum.

To date, there are no data specifically to evaluate the potential effect on groundwater due to leaching from gypsum piles (USEPA 1979a). Since gypsum wastes contain mainly calcium sulfate and lesser quantities of phosphates and fluorides, potential adverse effects may be regionally minimal (USEPA 1979a), but local contamination can be high.

2.1.2 Environmental Impact of Industry Wastes

Effluent guidelines were established for four primary factors and contaminants:

- phosphorus
- fluorides
- suspended solids
- pH

Air emission NSPS were established for:

- fluorides
- sulfur dioxide
- acid mist

These pollutants have been selected for direct control and monitoring because their harmful environmental effects have been well documented. The EID applicant should address the expected environmental impacts of these pollutants based on their magnitude and rates of discharge, and their effects interacting in the particular environmental setting.

Other pollutants in wastewater effluents have been identified as secondary parameters (USEPA 1974a):

- ammonia
- total dissolved solids
- temperature
- cadmium
- total chromium
- zinc
- vanadium
- arsenic
- uranium
- radium-226

These pollutants require monitoring, but specific effluent guidelines were not established because treatment of the primary factors and contaminants will also effect removal of the secondary, and because data sufficient to establish effluent limitations were lacking (USEPA 1974a). The applicant's EID should identify sources of the above and any other pollutants, expected discharges, and effectiveness of treatment techniques.

2.1.2.1 Human Health Impacts

The following listings summarize documented effects of primary and secondary pollutants on human health (USEPA 1974a).

Fluorides. Fluorides are rare in natural surface waters, but may occur in detrimental concentrations in groundwaters. Ingestion of fluoride compounds can result in:

- lowering of tooth decay in children - 0.8 to 1.5 mg/l fluoride ion in drinking water; but,
- mottling of tooth enamel in children, in quantities (varying with individuals) above 0.9 - 1.0 mg/l;
- endemic cumulative fluorosis and skeletal effects in adults, in (varying) quantities above 3 or 4 mg/l;
- death, or severe symptoms, in doses of 250-450 mg; severe symptoms are "diffuse abdominal pain; diarrhea and vomiting; excessive salivation, thirst, and perspiration; and painful spasms of the limbs" (National Academy of Sciences 1971).

Experts disagree on how much airborne fluoride is dangerous, but believe that levels equivalent to workplace heavy exposure would be required. Apparently airborne fluorides are largely retained when ingested, but the dangers of airborne fluorides include resettling and transport into drinking water or vegetable food supplies (National Academy of Sciences 1971).

Total Suspended Solids. Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. Besides the aesthetic displeasure associated with turbid waters or with bottom sludges when the suspended solids settle out, they can cause untreated water to be unpalatable and:

- suspended particles can absorb pesticide and other chemical impurities that might not be transported otherwise in the water.

pH (Acidity/Alkalinity). pH is a logarithnic expression of the concentration of hydrogen ions. At pH 7, hydrogen and hydroxyl (OH^-) ion concentrations in solution are essentially equal and the water is neutral. Lower pH values indicate acidity and higher values indicate alkalinity, in a nonlinear relationship. Extremes of pH are harmful or fatal to aquatic life, but human contact with pH in water is usually avoidable:

- a deviation of 0.1 pH unit from 7.0 may result in eye irritation to swimmers; appreciable irritation causes severe pain;
- by effects on plumbing fixtures, water lines, and water works structures, pH below 6.0 can cause high levels of iron, zinc, copper, cadmium and lead in drinking water.

Ammonia and Nitrate Nitrogen. Ammonia is a common product of the decomposition of organic matter. Dead and decaying animals and plants along with human and animal body wastes account for much of the ammonia entering the aquatic ecosystem. Ammonia exists in its non-ionized form only at higher pH levels and is the most toxic in this state. The lower the pH, the more ionized ammonia is formed and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other salts. The following direct and indirect stresses can accrue to human health:

- Sodium nitrate is a poisonous constituent of mineralized waters; potassium nitrate is more poisonous. Excess nitrates (500 mg consumed in one liter of water) cause irritation:
  - to mucous linings
  - to the gastrointestinal tract (symptom - diarrhea)
  - to the bladder (sympton - diuresis).
- Infant methemoglobinemia, can be caused by more than 10 mg/l (guideline) of nitrate nitrogen (NO_3-N) in water consumed; symptoms are:
  - blood disorders
  - cyanosis, a bluish discoloration of the skin, from inadequate blood oxygenation.

Total Dissolved Solids (TDS). In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances. Although TDS levels above 500 mg/l in drinking water are progressively unpalatable, levels of:

- 4,000 mg/l are unfit for human use, except in hot climates where the salt content may be tolerable;
- 5,000 mg/l in drinking water causes bladder and intestinal irritation.

Cadmium. Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment, as practiced in the United States, does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. Human health effects include:

- a severe bone and kidney syndrome reported in Japan, from ingestion of as little as 600 mg/day;
- as a cumulative toxicant, cadmium causes insidious chronic poisoning in mammals and also fish and probably other animals;
- organic compounds of cadmium may cause mutagenic or teratogenic (monstrous deformities) effects.

Chromium. In its various valence states chromium is hazardous to humans. The levels of chromate that are completely safe are so low as to prohibit determination. Effects of chromium include:

- lung tumors, from inhalation;
- skin sensitizations;
- in large doses,
  - corrosive effects on intestinal tract
  - inflamation of the kidneys.

Zinc. Zinc used in industry enters waste streams as both soluble and and insoluble salts. The soluble salts in drinking water at levels of 5 mg/l cause an undesirable taste that persists through conventional treatment. Zinc can have an adverse effect on man and animals at high concentrations.

Arsenic. Arsenic is found to a small extent in nature in the elemental form. It occurs mostly as arsenites of metals or as mineral pyrites. If ingested, arsenic compounds can be a sudden or a cumulative poison:

- 100 mg - severe poisoning
- 130 mg - possibly fatal poisoning
- Smaller doses can accumulate and be fatal - arsenic accumulates in the body faster than it is excreted.

Uranium and Radium-226. Radioactive materials present a host of hazards through direct exposure or by accumulation in the biological ecosystem. "Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism humans, fishes, and invertebrates. Beyond the obvious fact that radioactive wastes emit ionizing radiation, they are also similar in many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts.

"Radium-226 is one of the most hazardous radioisotopes of the uranium decay scheme, when present in water. The human body preferentially utilizes radium in lieu of calcium when present in food or drink. Plants and animals concentrate radium, leading to a multiplier effect up the food web.

"Radium-226 decays by alpha emission into radon-222, a radioactive gas with a half life of 3.8 days. The decay products of radon-222, in turn, are particulates which can be absorbed onto respirable particles of dust. Radon and its decay products has been implicated in an increased incidence of lung cancer in those workers exposed to high levels (Bureau of Mines, 1971). Heating or grinding of phosphate rock would liberate radon and its decay products to the surrounding atmosphere." (USEPA 1974a).

Guidelines for radiation exposure cannot be defined in terms of threshold values but it is agreed that exposure to radiation should be held to a minimun and should be encountered at all only when the necessity is justified.

2.1.2.2 Ecological and Environmental Impacts

Phosphorus. Increases of phosphorus in surface waters have been linked to a wide range of direct and indirect ecological disruptions. These include:

- proliferation of nuisance water plants;
- accelerated eutrophication of water bodies; and
- bioaccumulation and toxicity (of elemental P) for marine fish.

The plant overgrowth and eutrophication aspect of the effects of increased phosphorus availability have specific negative effects:

- dangerous to swimming, boating, and water skiing;
- interferes physically with sport fishing;
- interferes with development of fish populations;
- vile stenches and tastes associated with water;
- ineffectuates standard water treatment processes;
- aesthetic effects
    - reduced resort trade
    - lowered property values;
- contact rashes to human skin; and
- improved breeding environment for flies.

Fluorides. The effects of fluorides on the animal environment are related to vegetative accumulations and surface water contamination. Effects include:

- chronic fluoride poisoning of livestock when water contains 10-15 mg/l;
- shorter term fluoride poisoning of livestock when water ration contains 30-50 mg/l;
- toxicity to fish in concentrations above 1.5 mg/l.

The effects of acute poisoning in livestock include (National Academy of Sciences 1974):

- restlessness
- stiffness
- anorexia
- reduced milk production
- nausea and vomiting
- incontinence of urine and feces
- necrosis of mucosa of digestive tract
- weakness and severe depression
- cardiac failure

Chronic toxicosis is not always distinguishable from acute symptoms, but also results in (National Academy of Sciences 1974):

- debilitating osteoarthritis and lameness
- dental enamel lesions

Although milk production in livestock is affected, fluoride transfer to the milk is very slight. With poultry, however, a greater concentration of fluoride does show up in the eggs.

Suspended Solids. In the aquatic environment suspended solids cause a number of problems:

- turbid waters decrease photosynthetic activity of aquatic plants;
- settled solids on stream or lake beds
    - eliminate normal benthic species
    - reduce dissolved oxygen available in the area
    - stimulate populations of benthic sludgeworms and associated organisms.

pH Effects. Extremes or rapid fluctuations in pH level can create problems to aquatic organisms including:

- rapid death, and associated rotting of fishkills and generation of algal blooms;
- increased toxicity of other dissolved substances in the water, such as
    - matalocyanide
    - ammonia.

Ammonia and Nitrate Nitrogen. In the aquatic ecosystem, ammonia can lead to severe impacts:

- fish oxygen uptake is impaired and fish suffocate at 1.0 mg/l un-ionized ammonia;
- direct toxicity on all aquatic life in levels less than 1.0 mg/l to 25 mg/l, depending on pH and DO level;
- acceleration of eutrophication by supplying nitrogen through breakdown of ammonia.

Dissolved Solids. Dissolved solids levels in water affect aquatic organisms and in general make water troublesome to industrial uses and for irrigation. Effects on the ecosystem include:

- loss of habitat at 5,000-10,000 mg/l for species of freshwater fish;
- death to freshwater fish when salinity is changed rapidly;
- increased toxicity of heavy metals and organic compounds to fish and other aquatic life.

Temperature. Temperature is one of the most important and influential ecological water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development. Warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

The specific mechanisms and results of elevated temperature extremes include:

- higher chemical reaction rates;
- decreased DO;
- increased bacteria production;
- spawning perturbations;
- increases in predator, parasite, and competing species populations;
- fish food alterations;
- increased synergistic reactivity of pollutants;
- increase in green and blue-green algae and decrease in number and distribution of benthic organisms (food chain disruptions);
- in the presence of sludge, increased gas formation and multiplication of saprophytes and fungi.

Cadmium. Cadmium pollution problems are derived from direct toxicity and synergistic actions with other metals. These include:

- acute and chronic poisoning of aquatic and terrestrial species;
- increase synergistic toxicity of copper and zinc;
- concentration of cadmium in marine organisms, particularly molluscs.

Chromium. The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco, and sugar beets have been documented.

Zinc. Zinc is most toxic to aquatic organisms in soft water. Growth and survival of fresh- and saltwater species have been severely affected:

- 0.1 to 1.0 mg/l in soft water is lethal to fish;
- presence of copper in the water increases toxicity;
- but presence of calcium or hardness decreases the relative toxicity;
- invertebrate marine organisms are very sensitive - 30 μg/l retards growth of the sea urchin;
- marine environment problems include long-term sub-lethal effects of metallic compounds;
- zinc sulfate is lethal to many plants.

Vanadium. Vanadium and its compounds cause physiological disorders in mammals. The major concern is for effects in the aquatic ecosystem:

- the common bluegill fish can be killed by 6 ppm in soft water and by 55 ppm in hard water;
- other fish are similarly affected.

Arsenic. Arsenic ions and compounds can be lethal and harmful in both water and soil environments. Typical effects are:

- an accumulative poison in oysters and shellfish;

- arsenic trioxide is extremely harmful to some fish species (5.3 mg/l for 8 days);
- arsenic trioxide is lethal to mussels at 16 mg/l in 3 to 16 days;
- certain food crops are made unmarketable grown in water of 1 mg/l;
- soils containing 4-12 mg/kg are unproductive.

Uranium and Radium-226. The life spans of many animal species are not long enough to show adverse effects of low level radiation, but radionuclides tend to be accumulated in the food chain so that the greatest danger from radionuclides is to species high on the food chain. The potential effects for human health, or for economic disaster, are severe when food species accumulate potentially dangerous levels of radionuclides (resulting in a ban on production if controls are enforced). The most significant pathway to humans is through the accumulative effects on fish and shellfish, or through drinking water.

2.1.3 Other Impacts

2.1.3.1 Special Problems in Obtaining, Shipping, Storing, and Handling of Raw Materials and Products

In most instances potential major problems related to shipping, storing, and handling are well identified and systems are in place or methods available to keep these problems in check (1.5.2).

Continuing use of phosphate rock is assured and any special problems should be discussed that cause impacts related to the mining area, where the majority of the phosphate processing will be conducted. Phosphate mining in North Carolina is carried on adjacent to the Pamlico Estuary, below the water table. Cofferdams and pumps are used to expose phosphate deposits 100 feet deep. Even though the facility is well managed, eutrophication in the estuary occurs as the result of phosphate laden pumping waters being discharged to waters with significant nitrogen levels. The wastes of phosphoric acid production also are disposed in this high-water-level environment. Potential for leaching and for sedimentation and contamination of surface waters is high, especially in hurricane conditions.

In Florida, the significant special problems are related to new mining areas. The richer deposits still unmined lie below deeper overburdens and some deposits are in several layers. Higher volumes of overburdens must be moved and replaced. The effects of this problem on phosphate processing are less limiting, and the materials can be useful as supplies of sands and tailings for slime pond dewatering.

Effects of phosphate production on transportation facilities in new source industries should be assessed. Florida, North Carolina, and Gulf Coast facilities have good access to ocean, barge (river and intracoastal), pipeline, rail, and truck transportation. The EID should identify advantages of alternate transportation modes. When properly controlled, pipeline and barge transportation offer both environmental and economic advantages.

Since most facilities are near mines, stockpiles of phosphate rock are not necessary. Facilities that purchase phosphate rock should specify storage arrangements to prevent particulate air emissions and rainfall runoff of waters contaminated with phosphorus and TSP. When wet grinding is to be used the EID should detail whether storage will be exposed to the weather and what impacts of fugitive particulate emissions and runoff waters would be.

Ammonia and sulfur are normally stored in sealed tanks. The permit applicant's EID should address:

- administrative measures to deal with a catastrophic release;
- clean up and isolation techniques;
- collection and treatment systems;
- short-term and long-term effects of a spill on the soil and water ecosystems;
- human health impacts.

2.1.3.2 Special Problems in Site Preparation and Facility Construction

The environmental effects of site preparation and construction of new phosphate fertilizer manufacturing facilities are common to land disturbing activities on construction sites in general. Erosion, dust, noise, vehicular traffic and emissions, and some loss of wildlife habitats are to be expected and minimized through good construction practices wherever possible. At present, however, neither the quantities of the various pollutants resulting from site preparation and construction nor their effects on the integrity of aquatic and terrestrial ecosystems have been studied sufficiently to permit broad generalizations.

Therefore, in addition to the impact assessment framework provided in the USEPA document, Environmental Impact Assessment Guidelines for Selected New Sources Industries, the permit applicant should tailor the conservation practices to the site under consideration in order to account for and to protect certain site specific features that warrant special consideration (e.g., critical habitats, archaeological/historical sites, high quality streams, or other sensitive areas on the site). All mitigation/conservation measures that are proposed should be discussed in the EID.

Erosion Control During Construction. The major pollutant at a construction site is loosened soil that finds its way into the adjacent water bodies as sediment. Common remedial measures include, but are not limited to, proper planning at all stages of development and application of modern control technology to minimize the production of huge loads of sediment. Specific control measures include:

- the use of paved channels or pipelines to prevent surface erosion;
- staging or phasing of clearing, grubbing, and excavation activities to avoid high rainfall periods;
- the use of storage ponds to serve as sediment traps, where the overflow may be carefully controlled;
- the use of mulch or seeding immediately following disturbance.

If the applicant chooses to establish temporary or permanent ground cover, grasses normally are more valuable than shrubs or trees because of their extensive root systems that entrap soil. Grasses may be seeded by sodding, plugging, or sprigging. During early growth, grasses should be supplemented with mulches of wood chips, straw, and jute mats. Wood fiber mulch has also been used as an antierosion technique. The mulch, prepared commercially from waste wood products, is applied with water in a hydroseeder.

Site Selection Factors. The EID should include information to indicate the capacity of the soils and geology to accommodate production and waste storage. Problems which would require special consideration include:

- unstable soils;
- steep topography;
- presence of wetlands;
- location relative to floodplains;
- permeability of soils;
- erosion problems during construction and operation.

The applicant is responsible for assessing the effects of the proposed facility on groundwater quality and quantities. The areas of particular relevance to the phosphate manufacturing industry are:

- potential and effects of seepage of gypsum pond wastewaters into aquifers;
- potential for groundwater contamination from storage piles of raw materials and waste gypsum;
- use of groundwater for process and make-up water.

In western states water supply can be a limiting factor. The EID should evaluate effects of water consumption in terms of both groundwater and surface water supplies in the region.

2.1.4 Modeling of Impacts

The ability to forecast environmental impacts accurately often is improved by the use of mathematical modeling of the dispersion and dissipation of air and water pollutants as well as the effects of storm runoff.

Two of the most widely used and accepted models are:

- DOSAG (and its modifications);
- the QUAL series of models developed by the Texas Water Development Board and modified by Water Resources Engineers, Inc.

Some of the parameters that these models simulate are:

- dissolved oxygen
- BOD

- temperature
- pH
- solids
- phosphorus
- NH_3
- radioactive materials

Another model, extensively used in modeling estuaries is:

- RECEIV or RECEIV II, developed by Raytheon for the USEPA Water Planning Division.

The RECEIV models incorporate the salinity parameter.

In addition, there are many available water quality models that were developed in association with NPDES activity and the need for optimization of waste load schemes for an entire river basin.

There are also available mathematical models that have been used for air pollution studies and solid waste management optimization:

- for short-term dispersion modeling of point sources, EPA's PTMAX, PTDIS, and PTMTP models may be employed;
- for modeling of long-term concentrations over larger areas, the EPA Climatological Dispersion Model may be used for point and area sources.

The types of models to be used, their design, and the parameters to be modeled (or monitored for modeling) will vary in different USEPA regions, State jurisdictions, and air quality attainment areas. These details should be agreed upon between the regulating authority and the applicant early in the permitting stage. Even in instances when USEPA issues a "finding of no significant impact," and no EID is required, the processing of a PSD construction permit may still require air quality modeling and preconstruction monitoring.

In general, the use of mathematical models is indicated when arithmetic calculations are too repetitious or too complex. Their use also simplifies analysis of systems with intricate interaction of variables. Models thus offer a convenient way of describing the behavior of environmental systems.

3.0 POLLUTION CONTROL

NSPS have been established for air and water discharges based on USEPA surveys and tests (USEPA 1974a) of facilities in the phosphate subcategory, 40 CFR 418. These investigations include analyses of plant operating data and sampling of pollutant loadings in wastestreams. Standards of Performance are based on determinations of efficiency and attainability of pollution control technology and process options for existing and new facilities. New sources must attain discharge levels which are indicated as achievable using the "best practicable control technology currently available" (BPT). BPT is largely based on technology that was observed in facilities identified as "exemplary plants" in the USEPA study. "Standards of Performance Technology" refers to technological options which meet the NSPS. They may be the BPT's identified by USEPA in the development of the NSPS or they may be alternatives which meet the NSPS by other techniques. For wastestreams for which NSPS do not exist, technological control applications which represent the state of the art are of interest in the EID. The permit applicant must demonstrate that NSPS will be met. The sections which follow identify and describe typical Standards of Performance and state of the art technologies with which NSPS can be met.

3.1 STANDARDS OF PERFORMANCE TECHNOLOGY: END-OF-PROCESS CONTROLS AND EFFECTS ON WASTE STREAMS (AIR EMISSIONS)

3.1.1 Dust Control in Raw Materials Handling Operations

Enclosed operation and baghouses are typical methods of control at ground phosphate rock unloading stations. Satisfactory control of dust emissions from unloading hopper-bottom railroad cars or trucks is achieved by the use of flexible skirts around bases of the vehicles to contain dust and flexible-contact hoods to channel emissions to baghouses, which realize high efficiency in collection of this size particle (60% to 80% of the rock is less than 74 μm) (Slack 1968). Efficiencies are reported to be greater than 99% (USEPA 1979a).

Feed hoppers, storage bins, and conveyors are usually enclosed to reduce particulate emissions and moisture contamination of the rock. When transport of ground rock from storage bin to feed hopper is accomplished by pneumatic conveyors, a cyclone separator and baghouse are located at the destination for control of the bulk material and discharged dust (USEPA 1979a).

3.1.2 Control of SO_2 Emissions from Contact Process Sulfuric Acid Plants

There are a few physical mechanisms and many chemical means of removing SO_2 from gas streams. Almost any soluble alkaline material will absorb a significant fraction of SO_2 even in a crude scrubber. For years, sulfur dioxide has been removed from many process gases where the SO_2 adversely affected the product. The problems of removing SO_2 from acid plant gases are principally that of finding the least expensive mechanism consistent with minimal formation of undesirable by-products. The control processes in use by the sulfuric acid industry in those units installed since the promulgation of the NSPS (see Table 20) are reviewed below (USEPA 1978a).

3.1.2.1 Double Absorption Process

The double absorption process (used partially as the basis of the rationale for the SO_2 NSPS) has become the SO_2 control system of choice by the sulfuric acid industry since the promulgation of the NSPS. This process offers the following advantages over other SO_2 control process:

- As opposed to single absorption with scrubbing, a greater fraction of the sulfur in the feed is converted to sulfuric acid.
- There are no by-products.
- Contact acid plant operators are familiar with the operations involved.

The process, described in Section 1.3.2.1, builds in a second absorption tower to absorb SO_3 in the process gas and achieves at least 99.7% overall conversion of feed sulfur to sulfuric acid (USEPA 1978a). Double absorption offers the following operational advantages:

- permits higher inlet SO_2 concentrations than single absorption (second absorber handles residual SO_2 from first conversion step);
- higher inlet SO_2 concentrations allow reduced equipment size (partially offsetting cost of additional absorption equipment);
- spent acid or H_2S may be used as feedstock, with appropriate convential pretreatment;
- no reduction in on-stream production;
- needs no additional manpower.

3.1.2.2 Sodium Sulfite-Bisulfite Scrubbing

Tail gas scrubbing systems are generally applicable to all classes of contact acid plants. They can provide simultaneous control of SO_2 and to some extent SO_3 and acid mist. To date only the sodium sulfite-bisulfite scrubbing process has been demonstrated to be capable of meeting the SO_2 limit in the most cost effective manner. Other control processes such as ammonia scrubbing can meet the standard, but costs are relatively highly dependent on the marketability of by-products, i.e., ammonium sulfate, for which there may be little demand (USEPA 1978a).

In the Wellman-Power Gas process, the tail gases are first passed through a mist eliminator to reduce acid mist. Following mist removal, the SO_2 is absorbed in a three-stage absorber with a sodium sulfite solution. A sodium bisulfite solution results and is fed to a heated crystallizer where sodium sulfite crystals are formed and SO_2 gas and water vapor are released. The crystals are separated from the mother liquor and dissolved in the recovered condensate for recycle to the absorber. The recovered wet SO_2 is sent back to the acid plant (USEPA 1978a).

In all processes employing sulfite-bisulfite absorption even without regeneration, some portion of the sulfite is oxidized to sulfate, from which the sulfur dioxide cannot be regenerated in the heating sequence. This sulfate must be purged from the system. In the Wellman-Power Gas process, some thiosulfate is also formed. Apparently the extent of oxidation is dependent on several factors:

- oxygen content of the gas stream;
- the temperature and residence time of the liquor in the recovery sections;
- the presence of contaminants that may act as oxidation catalysts.

Despite the effectiveness of the sodium sulfite-bisulfite scrubbing process, none of the sulfuric acid plants installed since the promulgation of the NSPS have employed this process for tail gas SO_2 control (USEPA 1978a).

3.1.2.3 Ammonia Scrubbing

The ammonia scrubbing process uses anhydrous ammonia (NH_3) and water make-up in a two-stage scrubbing system to remove SO_2 from acid plant tail gas. Excess ammonium sulfite-bisulfite solution is reacted with sulfuric acid in a stripper to evolve SO_2 gas and produce an ammonium sulfate byproduct solution. The SO_2 is returned to the acid plant while the solution is treated for the production of fertilizer grade ammonium sulfate. The process is dependent on a suitable market for ammonium sulfate. Since the promulgation of the NSPS for sulfuric acid plants, one new plant (two units) and a new unit added to an existing plant, are employing an ammonia scrubbing system for tail gas SO_2 emmissions control (USEPA 1978a).

3.1.2.4 Molecular Sieve

This process utilizes a proprietary molecular sieve system in which SO_2 is absorbed on synthetic zeolites. The absorbed material is desorbed by purified hot tail gas from the operating system and sent back to the acid plant.

Since the promulgation of the sulfuric acid plant NSPS, one new unit has incorporated a molecular sieve system for SO_2 control in the original design. However, extensive operational difficulties with this system have caused this plant to be retrofitted with a dual absorption system for SO_2 control (USEPA 1978a).

3.1.3 Control of Acid Mist Emissions from Contact Process Sulfuric Acid Plants

Effective control of stack gas acid mist emissions can be achieved by fiber mist eliminators and electrostatic precipitators (ESP's). Although ESP's are frequently used in the purification section of spent acid plants, none are known to be in use in any new sulfuric acid plants. Even though ESP's have the advantage of operating with a lower pressure drop than fiber mist eliminators (normally less than 1 inch of H_2O), lack of application of this equipment to new sulfuric acid units is probably due primarily to its relatively large size and resultant high installation cost compared to fiber mist eliminators, and to the high maintenance cost required to keep the ESP's operating within proper tolerances in the acid environment, which is corrosive to the mild steel equipment.

Fiber mist eliminators utilize the mechanisms of impaction and interception to capture large to intermediate size acid mist particles and of Brownian movement to effectively collect micron to submicron size particles. Fibers used may be chemically resistant glass or fluorocarbon. Fiber mist eliminators are available in three different configurations (described below) covering a range of efficiencies required for various plants.

3.1.3.1 Vertical Tube Mist Eliminators

Tubular mist eliminators consist of a number of vertically oriented tubular fiber elements installed in parallel in the top of the absorber on new acid plants and usually installed in a separate tank above or beside the absorber on existing plants. Each element consists of glass fibers packed between two concentric 316 stainless steel screens. In an absorber installation the bottom end cover of the element is equipped with a liquid seal pot to prevent gas bypassing. A pool of acid provides the seal in the separate tank design. Mist particles collected on the surface of the fibers become a part of the liquid film which wets the fibers. The liquid film is moved horizontally through the fiber beds by the gas drag and is moved downward by gravity. The liquid overflows the seal pot continuously, returning to the process (USEPA 1978a).

Tubular mist eliminators offer a number of advantages and operate through a range of operating conditions:

- collection method
  - inertial impaction (particles greater than 3μ)
  - direct interception and Brownian movement (smaller particles:)
- gas velocity is low (6-12 m/min);
- volumetric flow is 28.3 standard cubic meters/minute (sm^3/min); 10-100 elements may be used depending on plant size;
- pressure drop - 13-38 cm (5-15 in) of water, higher drop for higher efficiency removing particles less than 3μ;
- usual efficiency
  - 100%, particles larger than 3 μ
  - 99.3%, particles smaller than 3 μ

Because the vertical tube mist eliminator does not depend only upon impaction for mist removal, it can be turned down (operated at a volumetric flow rate considerably below design) with no loss in efficiency. Available information indicates that the vertical tube mist eliminator is used in the great majority of new sulfuric acid units for acid mist control (USEPA 1978a).

3.1.3.2 Vertical Panel Mist Eliminators

Panel mist eliminators use fiber panel elements mounted in a polygon framework closed at the bottom by a slightly conical drain pan equipped with an acid seal pot to prevent gas bypassing. The polygon top is surmounted by a circular ring which is usually installed in the absorption tower and welded to the inside of the absorption tower head. Each panel element consists of glass fibers packed between two flat parallel 316 stainless steel screens. In large high velocity towers, recent designs have incorporated double polygons, one inside the other, to obtain more bed area in a given tower cross section (USEPA 1978a).

Operating and efficiency information for vertical panel mist eliminators follows:

- collection method - inertial impaction;
- gas velocity is somewhat high (120-150 m/min);
- pressure drop - 8 in of water;
- efficiency - 70 mg/m^3, equivalent to 0-375 lb/ton of 100% H_2SO_4.

These units are unsatisfactory for spent acid plants but usually find application in new dual absorption plants for acid mist removal from the intermediate absorber in order to afford corrosion protection for downstream equipment.

3.1.3.3 Horizontal Dual Pad Mist Eliminators

Two circular fluorocarbon fiber beds held by stainless steel screens are oriented horizontally in a vertical cylindrical vessel one above the other, so that the coarse fraction of the acid mist is removed by the first pad (bottom contactor) and the fine fraction by the other (top contactor). The bottom contactor consists of two plane segmented sections installed at an angle to the horizontal to facilitate drainage and give additional area for gas contact. The assembly may be located adjacent to or positioned on an absorption tower.

This unit uses the high velocity impaction mist collection mechanism, as does the panel mist eliminator; however, the collected acid drains downward through the pads countercurrent to the gas flow, producing a scrubbing action as well. Collected acid may be drained from external connections or returned directly to the absorber through liquid seal traps (USEPA 1978a).

Operating data for the horizontal dual pad mist eliminators are:

- collection method - high velocity impaction;
- superficial velocity - 2.7-3.0 m/s;

- pressure drop - 23 cm of water (9 in);
- efficiency - 70 mg/m^3 (0.375 lb/ton of 100% H_2SO_4) provided that a particle size distribution shows that this level can be met.

3.1.4 Control of Fluoride Emissions

3.1.4.1 Spray-Crossflow Packed Bed Scrubber

The spray-crossflow packed bed scrubber has been accepted for several years as the most satisfactory fluoride control device available for wet-process phosphoric acid plants. Most wet-process acid plants built since 1967 probably have installed this scrubber as part of the original design. During this same time, however, the spray-crossflow packed bed design has seen less general use in processes other than wet acid manufacture. The reluctance of the fertilizer industry fully to adopt the spray-crossflow packed bed scrubber can be traced primarily to concern about its operational dependability when treating effluent streams with a high solids loading. Such effluent streams can be handled by placing a venturi scrubber in series with and before a spray-crossflow packed bed scrubber. Also, improvements in spray-crossflow packed scrubber design have alleviated the initial problem of plugging and allow a greater solids handling capacity (USEPA 1977c).

The spray-crossflow packed bed scrubber consists of two sections - a spray chamber and a packed bed - separated by a series of irrigated baffles. Scrubber size will depend primarily upon the volume of gas treated. All internal parts of the scrubber are constructed of corrosion resistant plastics or rubber-lined steel. Teflon can be used for high temperature service. General maintenance consists of replacement of the packing once or twice a year. Both the spray and the packed section is equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations - particularly those rich in silicon tetrafluoride - are treated in the spray chamber before entering the packing. This preliminary scrubbing removes silicon tetrafluoride thereby reducing the danger of plugging the bed. At the same time, it reduces the loading on the packed stage and provides some solids handling capacity. Gases low in silicon tetrafluoride can be introduced directly to the packed section (USEPA 1977c).

The spray section accounts for approximately 40 to 50% of the total length of the scrubber. It consists of a series of countercurrent spray manifolds with each pair of spray manifolds followed by a system of irrigated baffles. The irrigated baffles remove precipitated silica and prevent the formation of scale in the spray chamber.

Packed beds of both cocurrent and crossflow design have been tried with the crossflow design proving to be the more dependable. The crossflow design operates with the gas stream moving horizontally through the bed while the scrubbing liquid flows vertically through the packing. Recycled pond water is normally used as the scrubbing liquor.

Typical operating data for spray-crossflow packed bed scrubbers include:

- pressure losses - 1-8 in of water, 4-6 in average;
- efficiency - 98.5 - 99.9% are attainable.

Table 28 lists the levels of fluoride control reached by several wet acid plants tested by the USEPA during the development of standards of performance. All plants used a spray-packed bed type scrubber to control the combined emissions from the reactor, the filter, and several miscellaneous sources and were felt to represent the best controlled segment of the industry. Gypsum pond water was used as the scrubbing liquid. Emission rates ranged from 0.002 to 0.015 pounds flouride (as F) per ton P_2O_5 input to the process.

Table 28. Scrubber performance in wet process phosphoric acid plants.

Plant	Scrubber design	Fluoride emmissions[a] (lb F/ton P_2O_5)
A	spray-cocurrent packed bed	0.015
B	spray-crossflow packed bed	0.006
C	spray-crossflow packed bed	0.002, 0.012[b]
D	spray-crossflow packed bed	0.011

[a] Average of testing results
[b] Second series of tests

Source: U.S. Environmental Protection Agency. 1977c. Final guidelines document: Control of fluoride emissions from existing phosphate fertilizer plants. Office of Air and Waste Management; Office of Air Quality Planning and Standards. Research Triangle Park NC, 274 p.

Spray-packed bed type scrubbers have seen only limited service in DAP and GTSP plants and none at all in run of pile TSP plants. Table 29 presents performance data, collected during the development of performance standards, for spray-crossflow packed bed scrubbers treating effluent streams from DAP and GTSP production, and GTSP storage facilities. In most cases, a preliminary scrubber (venturi or cyclonic) was used to reduce the loading of other pollutants (ammonia or solids) prior to treatment in the spray-crossflow packed bed scrubber. Gypsum pond water was used as the scrubbing solution except where indicated (USEPA 1977c).

3.1.4.2 Venturi Scrubbers

Venturi scrubbers are primarily particulate collection devices, however, they are also applicable to gas absorption work and are in widespread use throughout the phosphate fertilizer industry. They are particularly well suited for treating effluent streams containing large amounts of solids or silicon tetrafluoride because of their high solids handling capacity and self-cleaning characteristics. Operational reliability and low maintenance requirements are major reasons for the popularity of this scrubber design (USEPA 1977c).

A venturi provides a high degree of gas-liquid mixing, but the relatively short contact time and the concurrent flow of the scrubbing liquid tend to limit its absorption capabilities. When treating effluent streams requiring a high degree of fluoride removal, venturis are often used as the initial component in a multiple-scrubber system.

Two types of venturi scrubbers, gas actuated and water actuated, are in general use. In both cases, the necessary gas-liquid contacting is obtained from velocity differences between the two phases and turbulence in the venturi throat. Both types also require the use of a mist elimination section for removal of entrained scrubbing liquid. The major difference between the designs is the source of motive power for operating the scrubber. In the case of the gas actuated venturi, the velocity of the gas stream provides the energy required for gas-liquid contacting. The scrubbing liquid is introduced into the gas stream at the throat of the venturi and is broken

Table 29. Spray-crossflow packed bed scrubber performance in diammonium phosphate and granular triple superphosphate plants.

Type of facility	Sources controlled	Primary controls	Secondary controls	Fluoride emissions[a] (lb F/ton P_2O_5)
DAP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.034, 0.029[c]
DAP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.039
GTSP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel	3 spray-crossflow packed bed scrubbers in parallel	0.18, 0.06[c]
GTSP	reactor, granulator, drier, and cooler	process gases combined and sent to 2 venturi scrubbers in parallel followed by a cyclonic scrubber	spray-crossflow packed bed scrubber	0.21
GTSP storage	storage building	—	spray-crossflow packed bed scrubber	0.00036[d]

[a] Average of testing results.

[b] Weak phosphoric acid scrubbing solution.

[c] Second series of tests.

[d] Emission rate is in terms of pounds F per hour per ton of P_2O_5 in storage.

Source: U.S. Environmental Protection Agency. 1977c. Final guidelines document: Control of fluoride emissions from existing phosphate fertilizer plants. Office of Air and Waste Management; Office of Air Quality Planning and Standards. Research Triangle Park NC, 274 p.

into fine droplets by the accelerating gas stream. Pressure drop across the scrubber is generally high - from 8 to 20 inches of water. A fan is required to compensate for this loss in gas stream pressure (USEPA 1977c).

In a water actuated venturi, the scrubbing liquid is introduced at a high velocity through a nozzle located upstream of the venturi throat. The velocity of the water streams is used to pump the effluent gases through the venturi. Drafts of up to 8 inches of water can be developed at high liquid flow rates (USEPA 1977c).

The removal of the fan from the system makes the water acutated ventui mechanically simpler, more reliable, and less costly than the gas actuated type. An additional advantage is its relative insensitivity to variations in the gas stream flow rate. Gas actuated venturis rely upon the gas stream velocity for the energy for gas-liquid contacting, therefore, variations in the gas flow can greatly affect scrubber efficiency. The performance of the water-actuated venturi depends mainly on the liquid stream velocity.

Water actuated venturis find application principally as gas absorption units. Their use is usually limited, however, to small gas streams with moderate scrubbing requirements. The water-actuated venturi is seldom used for gas flows greater than 5,000 acfm because of the large water requirements (USEPA 1977c).

Performance data are available for venturi scrubbers installed in SPA and DAP plants. This information is presented in Table 30.

3.1.4.3 Spray Tower Scrubber

Spray towers provide the interphase contacting necessary for gas absorption by dispersing the scrubbing liquid in the gas phase in the form of a fine spray. Several types of spray towers are in general use. The simplest consits of any empty tower equipped with liquid sprays at the top and a gas inlet at the bottom. Scrubbing liquid is sprayed into the gas stream and droplets fall by gravity through an upward flow of gas. This design has the advantages of a very low pressure drop and an inexpensive construction cost but it can provide only about one transfer unit for absorption. Entrainment of scrubbing liquid is also a problem (USEPA 1977c).

Table 30. Venturi scrubber performance in superphosphoric acid and diammonium phosphate plants.

Type of Plant	Sources Controlled	Control System	Scrubbing Liquid	Fluoride Emissions[1.] (lb F/ton P_2O_5)
Vacuum evaption SPA	Barometric condenser, hotwell, and product cooling tank	Water actuated venturi	Pond water	0.0009
DAP	Reactor, granulator, drier, and cooler	3 gas actuated venturis in parallel	Weak acid (20-22% P_2O_5)	0.129

1. Average of testing results

Source: U.S. Environmental Protection Agency. 1977c. Final guidelines document: Control of fluoride emissions from existing phosphate fertilizer plants. Office of Air and Waste Management; Office of Air Quality Planning and Standards. Research Triangle Park NC, 274 p.

Cyclonic spray towers eliminate the excessive entrainment of scrubbing liquid by utilizing centrifugal force to remove entrained droplets. A tangential inlet is used to impart a spinning motion to the gas stream. Water sprays are directed parallel to the gas flow providing crossflow contacting of the gas and liquid streams. Pressure drops across the scrubber ranges from 2 to 8 inches of water. Solids handling capacity is high, however, absorption capacity is limited to about two transfer units (USEPA 1977c).

Fluoride removal efficiencies ranging from 84 to 95% have been reported for cyclonic spray towers treating wet acid plant effluent gases. Table 31 presents performance data obtained by USEPA for cyclonic spray towers installed in wet-process phosphoric acid, diammonium phosphate, and run of pile triple superphosphate plants. In most cases, the control system consisted of a primary venturi scrubber or cyclonic spray tower followed by a secondary cyclonic spray tower. Gypsum pond water was used as the scrubbing solution except where indicated.

Table 31. Cyclonic spray tower performance in wet process phosphoric acid, diammonium phosphate, and run of pile triple superphosphate plants.

Type of plant	Sources controlled	Primary controls	Secondary controls	Fluoride emissions[a] (lb F/ton P_2O_5)
WPPA	reactor, filter, and miscellaneous sources	two-stage cyclonic spray tower	—	0.056
DAP	reactor, granulator, drier, and cooler	3 cyclonic spray tower scrubbers in parallel. Scrubbers treating reactor-granular and drier gases use weak (28-30% P_2O_5) acid	2 cyclonic spray tower scrubbers in parallel treating reactor-granulator and drier gases	0.380
ROP-TSP	mixing cone, den, transfer conveyor, and storage pile	venturi scrubber	cyclonic spray tower scrubber with packed bed section	0.194, 0.211[b]
ROP-TSP	mixing cone, den, and storage pile	2 cyclonic spray tower scrubbers in parallel	2 cyclonic spray tower scrubbers in parallel	0.125

[a] Average of testing results

[b] Second series of tests

Source: U.S. Environmental Protection Agency. 1977c. Final guidelines document: Control of fluoride emissions from existing phosphate fertilizer plants. Office of Air and Waste Management; Office of Air Quality Planning and Standards. Research Triangle Park NC, 274 p.

3.2 STANDARDS OF PERFORMANCE TECHNOLOGY: IN-PROCESS CONTROLS AND EFFECTS ON WASTE STREAMS AND EMMISSIONS

3.2.1 Sulfuric Acid Plant Effluent Control

This technology is a process design modification which is installed to prevent accidental entry of contaminated water into surface drainage or sewage systems. The sulfuric acid plant has no process water effluent, and boiler blowdown is treated before discharge to the gypsum pond or to surface waters. Cooling coils in the cooling tower, are vulnerable to accidental break, causing rapid contamination of cooling water.

Process Description

The process involves installation and operation of the following facilities:

- a reliable pH or conductivity continuous monitor on either
  - combined non-contaminated plant effluent stream (preferred), or
  - cooling tower blowdown stream;
- a retaining area along the (usually) non-contaminated effluent stream capable of holding a 24 hour normal flow;
- a positive cutoff on the retaining area discharge point, such as a concrete abuttment fitted with a valve.

Optional features which could be built in are:

- lime treatment facilities at the retaining area;
- equipment for transferring the acid water from the retaining area to
  - a contaminated holding area, or
  - a recirculation system into an acid-consuming process.

When an acid break occurs an alarm sounds and the retaining area valve is shut (automatically is preferable). The plant necessarily will be shut down to locate and repair the leak. The contaminated water in the retaining area can be treated and neutralized, or be transferred to storage where it can be treated through central treating facilities, or be recirculated. If treatment is performed, the standard of performance is lime treatment, which can raise pH and also remove sulfate by precipitation of gypsum. The required pH standard is at least 6.

3.2.2 Wet Process Phosphoric Acid - Pond Water Dilution of Sulfuric Acid

The need to treat phosphate fertilizer process contaminated water is almost entirely dependent upon the local rainfall/evaporation ratio. Barring poor water management and concentrated periods of heavy rainfall, fresh water use and pond water evaporation should be essentially in balance. Any means of making an in-process change to reduce significantly fresh water use will create a negative water balance. In turn, this will eliminate the need for treatment of contaminated water and effect a no discharge condition.

The most effective way of attaining a negative water balance is to utilize contaminated water for dilution of sulfuric acid. The use of fresh water for this dilution step represents approximately 50% of the total fresh water intake to a phosphoric acid plant. Use of contaminated water for sulfuric acid dilution can:

- eliminate water effluent from the complex (except during extreme weather conditions);
- increase overall P_2O_5 recovery by the amount of P_2O_5 in the contaminated water.

Two methods for successfully using contaminated water exist. Both are proprietary. One is a trade secret; the other is protected by patent.

The trade secret procedure involves two key points:

1. a mechanical means to effect dilution without pluggage of process equipment;
2. redesign of the phosphoric acid reactor cooling system to remove the heat load formerly removed by the sulfuric acid dilution cooler.

The patented process involves sulfuric acid dilution by a two-step procedure in a manner radically different from current practice. The details of process control, vessel design, and materials are all proprietary information.

3.2.3 Ammonium Phosphate Self-Contained Process

The best means of reducing NH_3-N in the contaminated water system is to prevent its entry into the water. NH_3-N enters the contaminated water principally through the ammonium phosphate plant gas scrubber system. A secondary entry point is washdown or water spillage into a surface drainage system. These sources can be segregated from the gypsum pond water system and can be either introduced back into the process or treated for ammonia removal prior to discharge into the gypsum pond.

One means of doing this is to adjust the in-process water balance to permit the absorption of the collected water containing NH_3-N. The degree of water balance adjustment is dependent upon the quantity of water in the two identified streams. Reduction of these water streams to a minimum may require design changes to maximize scrubber water recirculation.

The principal means of adjusting the ammonium phosphate process water balance is to increase the concentration of the phosphoric acid feed used in the plant. In conventional processes 30-40% P_2O_5 phosphoric acid is required to produce ammonium phosphates. It may be necessary to increase this concentration to as high as 54% P_2O_5. This is dependent upon the water quantity to be absorbed and the acid concentration required to produce the specific ammonium phosphate product.

The TVA pipe reactor and pipe-cross reactor have been demonstrated effective in meeting these criteria. 54% P_2O_5 acid is used and dust-laden (and fluorine-laden) contaminated water is returned to the product and leaves the plant as product (Lee and Waggoner 1975). The remaining water in scrubber liquor is flashed off in the granulator or stripped out by airflow through the cooler.

3.3 STANDARDS OF PERFORMANCE TECHNOLOGY: END-OF-PROCESS CONTROLS AND EFFECTS ON WASTE STREAMS (WASTEWATER EFFLUENTS)

3.3.1 Gypsum Pond Water Treatment

The closed-loop contaminated water stored in the gypsum pond must be treated prior to any discharge necessitated by unusually high rainfall (which should be in excess of the local 24-hour 25-year frequency event). Once the storage area approaches capacity it is necessary to begin treating the contaminated water for subsequent discharge to natural drainage bodies.

Treatment must accomplish NSPS levels for phosphorus, fluorides, and total suspended solids (TSS). In most cases pH is also regulated through the NPDES permit. "Double liming," or a two stage lime neutralization is the standard of performance procedure.

The first treatment stage provides sufficient neutralization to raise the contaminated water (containing up to 9000 mg/l F and up to 6500 mg/l P) from pH 1-2 to pH 3.5-4.0. The resultant treatment effectiveness is largely dependent on constancy of the pH control. At a pH level of 3.5 to 4.0, the fluorides will precipitate principally as calcium fluoride (CaF_2) by the following reaction:

$$H_2SiF_6 + 3CaO + H_2O \rightarrow 3CaF_2 + 2H_2O + SiO_2$$

This mixture is held in a quiescent area to allow the particulate CaF_2 to settle.

Equipment used for neutralization ranges from crude manual distribution of lime with localized agitation to a well engineered lime control system with a compartmented mixer. The quiescent areas range from a pond to a controlled settling rate thickener or settler. The partially neutralized water following separation from the CaF_2 (pH 3.5-4.0) now contains 30-60 mg/l F and up to 5500 mg/l P. This water is again treated with lime sufficient to increase the pH level to 6.0 or above. At this pH level calcium compounds, of CaF_2, precipitate from solution. The primary reactions are shown by the following chemical equation:

$$2H_3PO_4 + CaO + H_2O \rightarrow Ca(H_2PO_4)_2 + 2H_2O$$
$$Ca(H_2PO_4)_2 + CaO + H_2O \rightarrow 2CaHPO_4 + 2H_2O$$

As before, this mixture is retained in a quiescent area to allow the $CaHPO_4$ and minor amounts of CaF_2 to settle.

The reduction of the P value is strongly dependent upon the final pH level, holding time, and quality of the neutralization facilities, particularly mixing efficiency. Figure 39 shows a sketch of a well designed "double lime" treatment facility.

Laboratory and plant data for response of phosphorus and fluoride concentrations to pH levels are presented below:

pH	Phosphorus (mg/l)		Fluoride (mg/l)	
	laboratory	plant	laboratory	plant
5.5	-	-	-	17
6.0	-	42	-	14
6.5	-	24	-	12.5
7.0	500	18	13	12.5
7.5	330	14	8.5	12.5
8.0	200	12	6.8	12.5
8.5	120	8	5.8	12.5
9.0	20	6	5.2	12.5
9.5	3	3	4.8	12.5
10.0	1.2	1.2	4.6	12.5

Source: U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs. Washington DC, 168 p.

Although the starting concentrations are either arbitrary or specific to certain plants tested by USEPA, the data show that P and F are removed in significant amounts at higher pH.

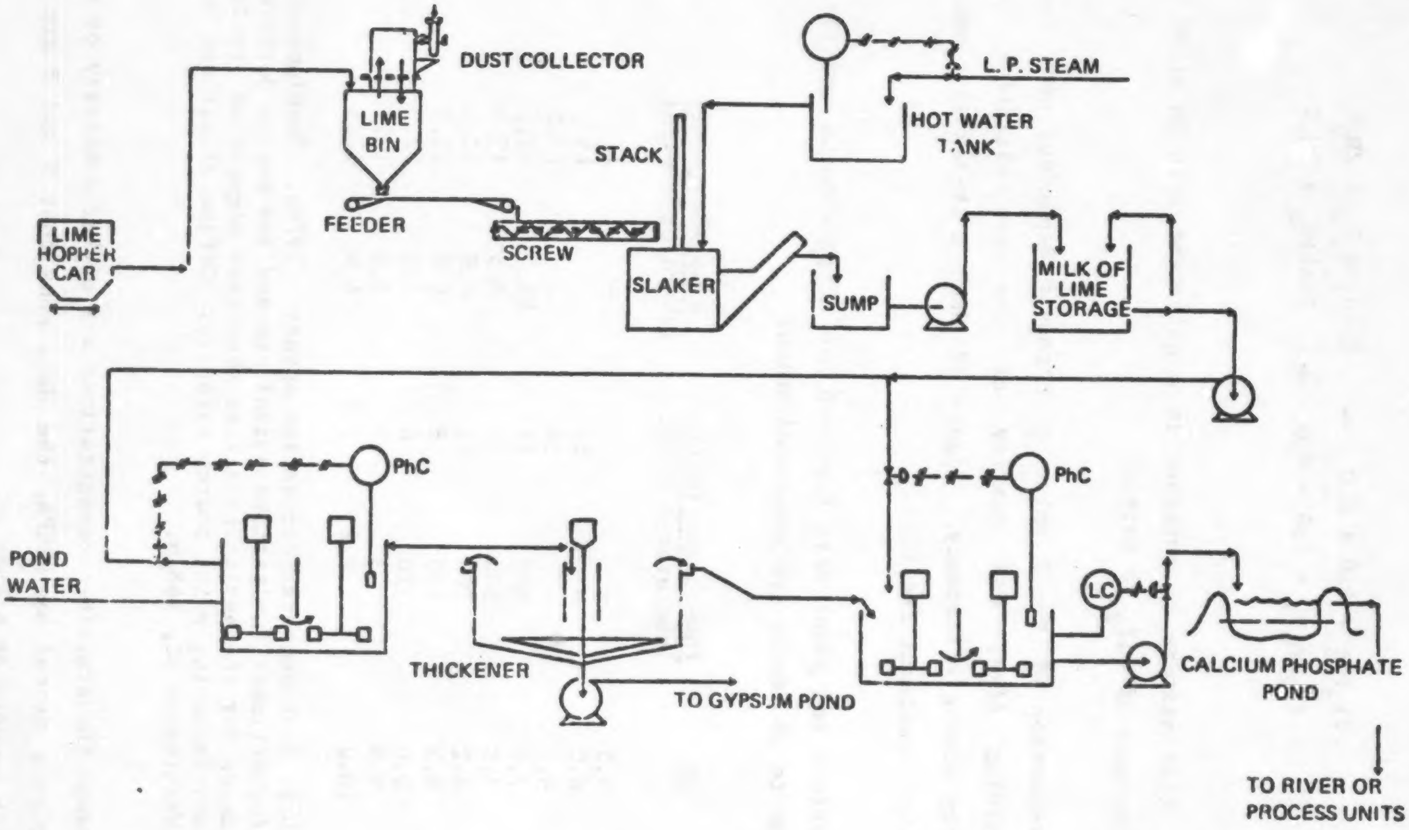

DUST COLLECTOR
LIME BIN
FEEDER
SCREW
LIME HOPPER CAR
STACK
SLAKER
HOT WATER TANK
L. P. STEAM
SUMP
MILK OF LIME STORAGE
PhC
PhC
POND WATER
THICKENER
TO GYPSUM POND
LC
CALCIUM PHOSPHATE POND
TO RIVER OR PROCESS UNITS

Figure 39. Pond water treatment system.

Source: U.S. Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs. Washington DC, 168 p.

Data from one plant tested (USEPA 1974a) show that phosphorus concentrations also decrease with time once pH ranges above 5 are met. When a 46-hour holding period was employed, the following values were derived:

pH	Phosphorus (mg/l)
5.8	20
6.5	9.1
8.3	3.6

The time effect on phosphorus concentration is:

Time-hours	pH	Phosphorus (mg/l)
0	7.85	60
5	7.6	29
22	6.7	19
46	6.4	9

Data from three years of double lime treatment of gypsum pond effluent from one plant at a pH of 5 to 7 show a phosphorus concentration (as P) of 10 to 40 mg/l.

Radium-226 is also precipitated by lime treatment incrementally with increasing pH as presented below (USEPA 1974a):

pH	Radium-226 (picocuries/l)
2.0 (sic)	91
1.5 (sic)	65
4.0	7.6
8.0-8.5	0.04

Double liming is not effective in controlling NH_3-N in contaminated water. This is why the self-contained ammonium phosphate NSPS has been established. There is no acceptable method of economically removing NH_3-N from aqueous solutions as weak as 20-60 mg/l. It is instead most important to keep NH_3-N from entering the contaminated water system.

3.3.2 Gypsum Pond Water Seepage Control

The contaminated (gypsum pond) water storage areas are surrounded by dikes except when mining pits are used. The base of these dikes are normally natural soil from the immediate surroundings. When height of the retaining dikes must be increased, gypsum from inside the diked area is added to the top of the earthen base. Dikes in Florida now extend 100-120 ft in vertical height and tend to have continual seepage of contaminated water through them. To prevent this seepage from reaching natural drainage streams, it should be collected and returned to the pond.

Figures 40 and 41 illustrate the design and use of a seepage collection ditch around the perimeter of the diked area. The ditch should be of sufficient depth and size to collect contaminated water seepage and to permit collection of seepage surface water from the immediate outer perimeter. This is accomplished by erection of a small secondary dike. The secondary dike also serves as a back-up or reserve dike in the event of a failure of the major dike.

The design of the seepage ditch in respect to distance from the main impounding dike and depth is a function of the geology of the area and the type material used for the dike. Some data suggest that the gypsum pond bottoms tend to be self-sealing (Wissa 1977). That is, compacted gypsum plus clay fines and aluminum and iron silicates forced into the interstices may form an artificial "cement" like layer on the bottom of old gypsum ponds which is both acid resistant and of very low permeability. In the design of gypsum ponds and ditches the applicant must consider the area geology and the phreatic water level of the impounding dike material to achieve an effective seepage control system. Water table aquifers, and conceivably deeper aquifers, have been contaminated in the vicinity of ponds (TRC 1979). An installation of a pump station at the low or collection point of the seepage ditch is an essential part of the seepage control system. (USEPA 1974a).

3.3.3 Other End-of-Process Controls

It is reportedly possible for a fertilizer plant to meet the no-discharge criterion without the use of gypsum ponds for storage. One

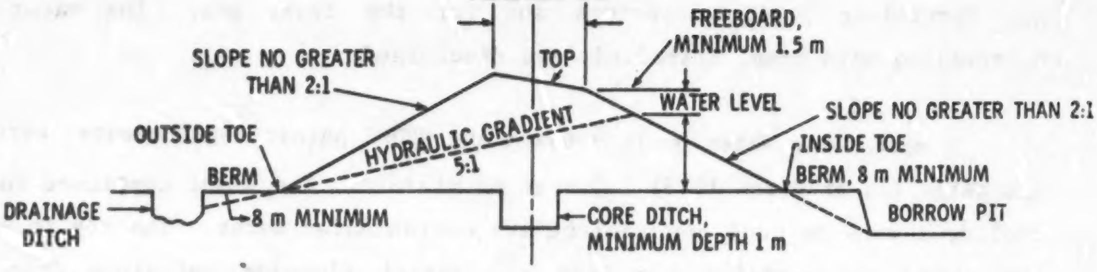

MINIMUM 6 m
FREEBOARD, MINIMUM 1.5 m
SLOPE NO GREATER THAN 2:1
TOP
WATER LEVEL
SLOPE NO GREATER THAN 2:1
OUTSIDE TOE
HYDRAULIC GRADIENT 5:1
INSIDE TOE
BERM
BERM, 8 m MINIMUM
DRAINAGE DITCH
8 m MINIMUM
CORE DITCH, MINIMUM DEPTH 1 m
BORROW PIT

Figure 40. Recommended minimum cross section of dam.

Reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc., Year of first publication 1968.

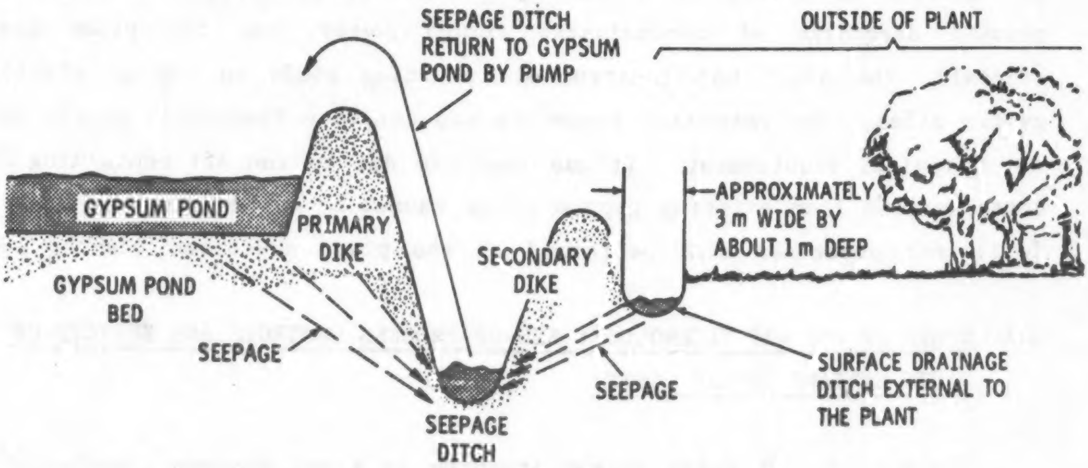

SEEPAGE DITCH RETURN TO GYPSUM POND BY PUMP
OUTSIDE OF PLANT
GYPSUM POND
PRIMARY DIKE
APPROXIMATELY 3 m WIDE BY ABOUT 1 m DEEP
SECONDARY DIKE
GYPSUM POND BED
SEEPAGE
SURFACE DRAINAGE DITCH EXTERNAL TO THE PLANT
SEEPAGE
SEEPAGE DITCH

Figure 41. Gypsum pond water seepage control.

Source: Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC, 168 p. in USEPA 1979a.

plant along the Houston Ship Channel in Texas has claimed success by use of process modifications tailored to its operation (Mabrey 1978). This plant operates on a relatively small sight and previously took advantage of once-through channel water (10,000-12,000 gpm) to cool the evaporator and barometric condenser, and to supply scrubber water for the phosphoric acid and fertilizer product reactors and for the dryer gas. The water was neutralized with lime, clarified, and discharged.

To meet Texas Water Quality Board and NPDES permit requirements, zero discharge (as of March 1978) had been maintained. The plant continues to use cooling towers to cool and recirculate contaminated water. The key to using the towers successfully has been to control fluoride emissions from the phosphate fertilizer processes contaminated wastwater, with pH of 1-3 and fluoride concentrations of 4000-5000 ppm at equilibrium (Mabrey 1978). NSPS fluoride emission levels reportedly have been achieved by adjusting the ratio of fluoride to silica in a company classified procedure. Meanwhile, to prevent discharge of contaminated runoff water from the piles due to rainfall, the plant has constructed retaining ponds on top of stabilized gypsum piles. The retaining procedure has not been thoroughly proven and is not a typical requirement. It was required due to run off containing NH_3-N contamination from existing gypsum piles caused by wastes from non-phosphate fertilizer processes also performed at the plant described (Mabrey 1978).

3.4 STATE OF THE ART TECHNOLOGY: END-OF-PROCESS CONTROLS AND EFFECTS ON WASTE STREAMS (SOLID WASTE)

The quantity of waste gypsum produced in a wet process phosphoric acid plant ranges from 4.6 to 5.2 metric tons gypsum/metric ton P_2O_5 produced (Slack 1968). Approximately 1,360 m^3 of gypsum will be accumulated yearly per metric ton of P_2O_5 produced per day; at least 2,230 m^2 of land area per daily metric ton P_2O_5 should be reserved for gypsum disposal (USEPA 1979a).

In the United States and other locations three disposal practices are currently used: gypsum ponds and piles, abandoned mine pits, and sea disposal (USEPA 1979a).

3.4.1 Disposal in Gypsum Ponds and Piles

In the United States more than 90% of the phosphate fertilizer plants use gypsum ponds to collect the slurry. Initially, two or more areas are converted to lagoons by means of low dikes provided with proper outfalls for potential effluent discharge. As one area becomes filled, the gypsum stream is diverted to the second area, and the first section is allowed to dry out sufficiently to support mechanical equipment. The dike is then increased in height, using deposited gypsum as the source of material, and the procedure is repeated. An alternative is the use of draglines to stack wet gypsum from the gypsum flats area of the pond onto an active gypsum pile to dry (USEPA 1978c). Existing gypsum piles range in height from 30 m to 36 m (100-120 ft) (USEPA 1979a).

In the western states where poor land stability or availability prevents the use of gypsum ponds, gypsum cake from the vacuum filters is transported by conveyor to gypsum stacks (USEPA 1979a).

3.4.2 Disposal in Abandoned Mine Pits

This disposal technique is practiced primarily in Florida. Instead of constructing gypsum ponds, abandoned phosphate rock surface mines are used as gypsum ponds and for other solid residue disposal. A potential environmental hazard from this disposal technique is the possible leaching of fluorides and phosphates into the groundwater system. Because the mined-out pits are closer to subsurface aquifers, their potential for adverse environmental effects is greater than that of the surface gypsum ponds (USEPA 1979a).

3.4.3 Disposal in Sea Outfalls

This disposal technique, used by less than 2% of the phosphate fertilizer plants in the United States, but more widely used throughout Europe, is practiced at plants located in coastal areas. Gypsum is pumped into the ocean or, in a few cases, discharged into major rivers. After removal from the vacuum filter, the gypsum is slurried with about a tenfold quantity of seawater or cooling water (Slack 1968, USEPA 1979a).

Seawater is a better solvent for gypsum than fresh water. The solubility of gypsum in seawater is about 3.5 g/l as compared to about 2.3 g/l in fresh water. The solids content of the gypsum slurry is below 5%, low enough for quick dispersion and dissolution in ocean water (Slack 1968, USEPA 1979a).

3.4.4 Resource Recovery

Soil Treatment

In 1975, approximately 30 x 10^6 metric tons of gypsum waste were generated by the phosphate fertilizer industry. Of this total, about 90 x 10^3 metric tons were applied to calcium-deficient soil in the southern states for peanut growing. Gypsum was also used for improvement of alkali soils in California and for land reclamation in coastal areas. It conditions the soil and causes sodium chloride to leach out faster (USEPA 1979a). Since gypsum waste contains varying quantities of phosphoric acid, it also serves as a light fertilizer.

Wallboard Problems

Waste gypsum has been used for wallboard. In the United States, the dihydrate process for phosphoric acid production produces a gypsum waste high in phosphoric acid, which results in poor quality wallboard. Also, there is some concern about the possible low-level radiation effects from wallboard made of uranium- and radon-containing gypsum wastes.

In Europe and Japan, where the hemihydrate process is more commonly used, the resulting gypsum waste is purer, containing less phosphoric acid and uranium. More of this gypsum waste is used for wallboard. In England, where only the standard dihydrate process is used, special purification methods make the by-product suitable for wallboard. This purification step is more economically feasible in England than in the United States, because natural (and purer) gypsum is not as abundant in England as it is in the United States (USEPA 1979a).

Cement Supplement Problems

Another possible use for gypsum is in cement and other road toppings. However, the phosphoric acid and other phosphates retard setting and lower the strength of the hardened body. Fluorine compounds reduce setting time and lower the concrete strength, but these effects are small compared to the effects of phosphate contamination. In Florida, there are further concerns over public exposure to low level radiation from road surfaces containing gypsum wastes or from road base material containing phosphate rock mining overburden (USEPA 1979a).

Ammonia and CO_2 Treatment

Gypsum can be reacted with ammonia and carbon dioxide to form ammonium sulfate and calcium carbonate. This is an old and well-known practice applied to natural gypsum, but there has been relatively little application to by-product gypsum. Only a few plants in India, Japan, and Europe use this technology (USEPA 1979a).

Silica Thermal Treatment

Another potential resource recovery method is treating by-product gypsum with silica at high temperatures to produce sulfuric acid. The additional product of calcium silicate could be used for cement. Although the method is technically feasible, the high water content of gypsum, the corrosive effect of fluorides, and the adverse effect of P_2O_5 content on cement quality are all major drawbacks. Also, due to the price and availability of sulfur in the United States, this technology is not yet economically feasible (USEPA 1979a).

3.5 POLLUTION CONTROL RECOMMENDATIONS EXCERPTED FROM THE CENTRAL FLORIDA PHOSPHATE INDUSTRY FINAL AREAWIDE ENVIRONMENTAL IMPACT STATEMENT

The recently published Areawide EIS for the central Florida phosphate industry lists several recommended practices which are anticipated to be required for new source phosphate fertilizer facilities in central Florida.

Because of the concentration of the industry in that area, and because of their potential relevance to future policy determinations, the recommendations are included below. These recommendations are included for information only, and are not to be taken as final policy. The applicant is advised to coordinate the scope of the EID with the regional USEPA officials in all cases, prior to starting work.

USEPA Region IV Phosphate Fertilizer Facility Recommendations

- Meet Federal air quality new source performance standards and design surge capacity in the USEPA Standards of Performance for New Sources for process water systems.
- Line gyp ponds[1] with an impervious material unless it can be demonstrated in the site-specific EIS that such lining is unnecessary in protecting ground water from chemical and radiological contamination.
- Recirculate process and non-process water. The non-process system should have the same design surge capacity as required in the Standards of Performance for New Sources for process water systems.
- Provide for recovery of fluorine compounds from phosphoric-acid evaporators unless it is determined at the time of permit application that market conditions are such that the cost of operation (not including amortization of initial capital cost) of the recovery process exceeds the market value of the product. If there is an exception, the site-specific EIS is to contain an estimate of pond-water fluoride concentrations to be attained and levels of fluorine emission. Estimated fluorine emissions from new source gyp ponds should not cause the plant complex to exceed the total allowable point source fluorine emissions within the plant complex if a permit is to be issued.
- Encourage recovery of uranium based on economic feasibility data to be included in the site-specific EIS.

[1] Shortened term: gypsum ponds.

Source: U.S. Environmental Protection Agency. 1978q. Final areawide environmental impact statement, Central Florida phosphate industry, Volume 1. EPA 904/9-78-26a. Atlanta GA, 80 p.

4.0 OTHER CONTROLLABLE IMPACTS

4.1 AESTHETICS

New source phosphate facilities may involve large and complex operations occupying hundreds of acres. Rock storage and handling areas, haul roads, rock conveyors, and slurry pipelines, gypsum ponds and piles, dust, erosion, and sediment-laden streams are aesthetically displeasing to many. Particularly in rural and suburban areas, phosphate fertilizer manufacturing (and possible associated mining activity) can represent a noticeable intrusion on the landscape. Measures to minimize the impact on the enviornment must be developed during site selection, plant planning design, and reclamation. The applicant should consider the following factors where feasible to reduce potential aesthetic impacts:

- Existing Nature of the Area. The topography and major land uses in the area of the candidate sites are important. Topographic conditions, and existing trees and vegetation visual barriers can be used to screen the operation from view. A lack of topographic relief and vegetation would require other means of minimizing impact, such as regrading or planting of vegetation buffers;
- Proximity of Parks and Other Areas Where People Congregate for Recreation and Other Activities. The location of public use areas should be mapped and presented in the EID. Representative views of the plant site from observation points should be described. The visual effects on these recreational areas should be described in the EID in order to develop the appropriate mitigation measures;
- Transportation System. The visual impact of new access roads, rail lines, haul roads, barge docking, pipelines, and storage facilities, the landscape or waterfront should be considered. Locations, construction methods and materials, and maintenance should be specified.

4.2 NOISE

The major sources of noise associated with phosphate fertilizer manufacturing include:

- Plant construction equipment (bulldozers, graders).
- Rock transport systems (haul roads, conveyors, pipelines, loading dozers).
- Rock grinding and handling.
- Boilers and steam venting.
- Product transport systems (truck, railroad and barge loading).
- Land reclamation/grading equipment.

These activities can create significant ambient noise levels that may decrease with increasing distance from the site. Noise can be attenuated effectively with thick stands of vegetation or other barriers. Even at distances of 1,500 to 2,000 feet the increases in noise levels due to manufacturing activities still may be noticeable. Noise receptors within a half mile of the source are the most pertinent for most facilities and should be documented in the EID.

Noise also can create serious health hazards for exposed workers; therefore, the necessary source and operational control methods should be employed.[1] Such measures include:

- Enclosed process machinery.
- Mufflers on engines.
- Lined ducts.
- Partial barriers.
- Vibration insulation.
- Imposed speed limits on vehicles.
- Scheduled equipment operations and maintenance.

A suitable methodology to evaluate noise generated from a proposed new source facility would require the applicant to:

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[1] USEPA has recommended a 75-dBA, 8-hour exposure level to protect from loss of hearing, and a 55-dBA background exposure level to protect from annoyance of outdoor activity.

- Identify all noise-sensitive land uses and activities adjoining the proposed plant site.
- Measure the existing ambient noise levels of the areas adjoining the site.
- Identify existing noise sources, such as traffic, aircraft fly-over, existing mining and other industry, in the general area.
- Determine whether there are any State of local noise regulations that apply to the site.
- Calculate the noise level of the manufacturing processes, compare that value with the existing area noise levels and the applicable noise regulations.
- Assess the impact of the operation's noise and, if required, determine noise abatement measures to minimize the impact (quieter equipment, noise barriers, improved maintenance schedules, etc.)

4.3 ENERGY SUPPLY

Cogeneration in industrial processes denotes any form of the simultaneous production of electrical or mechanical energy and useful thermal energy (usually in the form of hot liquids or gases) (USDOE 1978).

The permit applicant should evaluate the energy efficiencies and demands of all methods considered during project planning in the context of an alternative analysis. Also, feasible design modifications should be considered in order to reduce energy needs.

At a minimum, the applicant should provide the following information in the EID:

- Total external energy demand for operation of the mine.
- Total energy generated on site.
- Energy requirements by type.
- Source of energy off-site.
- Proposed measures to conserve or reduce energy demand and to increase efficiency of mine operation.

4.3.1 Cogeneration

Phosphate complexes which produce sulfuric acid on site obtain, due to the exothermic combustion and absorption reactions, a net yield of energy in the form of moderate pressure steam. This steam is usually used to generate the major on-site electrical energy requirements. After generation of electricity, process steam amounts to about 1,900,000 Btu per ton of 100% sulfuric acid (Blouin 1975). Highly integrated complexes which produce wet process phosphoric acid, SPA, and/or conventional process granulated fertilizer products may consume this energy for steam ejectors, vacuum evaporators, dryers, or steam powered machinery. The EID should indicate the power demands of processes to be used and assess potential for excess steam capacity for cogeneration of marketable electric power. Process options, such as melt-type ammoniator-granulators should be considered in view of the potential for converting energy savings from unneeded dryers into power generation. The Public Utility Regulatory Policies Act of 1979 provides for Federal Energy Regulatory Commission rules favoring cogeneration facilities, and requiring utilities to buy or sell power from qualified cogenerators at just and reasonable rates.

4.3.2 Energy Consumption and Conservation

In 1976 the energy consumption in the U. S. was about 74 x 10^{15} Btu (quads) per year. The U. S. Federal Energy Administration and U. S. Department of Agriculture estimated the energy consumption in fertilizer production to be 0.621 quad per year. Blouin and Davis' estimate for the chemical fertilizer industry energy consumption was 0.522 quad per year. Thus 0.7 - 0.8% of the nation's energy goes for fertilizer production. Table 32 indicates that roughly 68% of that energy consumption is to for ammonia production, and about 12% for phosphate fertilizer.

Although the phosphate fertilizer industry accounts for a small portion of total energy consumption, energy conservation practices are of benefit to the producer, the regional energy supply, and the U.S. economy.

Table 32. Energy for fertilizer nutrient production.[a]

Nutrient	Energy requirement, Btu's per pound
N	28,000
P_2O_5	5,000
K_2O	4,000
S	4,000[b,c]

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a. Source: White, Bill. 1977. Fertilizer cost trends - energy, environment, transportation. Fertilizer Progress, Volume 8. January-February 1977 in Barber 1978a.

b. Energy for Frasch mined sulfur

c. Source: Blouin, Glenn M. and Charles H. Davis. 1975. Energy requirements for the production and distribution of chemical fertilizers in the U.S. Energy and Agriculture, Proceedings of a workshop. Southern Regional Educational Board. Atlanta GA, p. 51-67 in Barber 1978a.

Conservation practices applicable to the phosphate fertilizer industry are described below (Barber 1978a):

- Wet grinding of phosphate rock instead of dry grinding conserves energy. Phosphate drying consumes energy and results in the discharge of particulates and operation of abatement equipment.
- Melt-type granulation processes eliminate drying of granulated fertilizer. Energy is conserved by eliminating the drying step and by decreasing the volume of air to be treated for air pollution control.
- Emission of dust from granulation processes is reduced by making strong granules. Formation of particulates from handling is held to a minimum and dust control simplified.
- The pipe reactor installed in ammoniator-granulators eliminates formation of small particulates and reduces the volume of gas to be treated. Otherwise, high pressure drop scrubbers (about 50 inches of water) are necessary to meet air emission standards.

- Particulate collecting systems are designed to provide optimum dust pickup and transport velocities. Long and complicated ducts give rise to duct stoppages or expenditure of excessive energy to transport dust at high enough velocity to prevent stoppages.

- Baghouse collectors are used instead of scrubbers for particulate collection when the particulates have low hygroscopicity and the gas temperature does not exceed the limit for fabric filters. Baghouse collectors consume less energy than scrubbers unless gases have to be heated to overcome the hygroscopicity problem. When the gases have to be heated, energy for baghouses and scrubbers is about the same.

- Effluent from granulation processes may be reused in the process or the effluent may be sold as a fluid fertilizer. This saves energy for nutrient production and eliminates a waste treatment facility.

In addition, well planned siting of the fertilizer plant can greatly affect net energy consumption of the operations. The amount of energy consumed in transportation by the four major transportation modes is shown below in Btu's/ton-mile (Achorn & Kimbrough 1978):

Pipeline	450
Barge	500
Rail	700
Truck	2,500-2800

These data indicate that to conserve energy, the applicant should use pipeline, barge, and perhaps rail as much as possible, and avoid truck transportation.

Finally, uranium production, which can have significant effects on energy supply, should be considered. This practice can help toward making phosphate fertilizer manufacturing a net producer rather than consumer of energy.

4.4 SOCIOECONOMICS

The introduction of a large new phosphate fertilizer facility into a community may cause land use, economic, and social changes. Therefore, it is necessary for an applicant to understand the types of impacts or changes that may occur so that they can be evaluated adequately. The importance of these changes usually depends on the size of the existing community where the facility is located. The significance of the changes caused by a facility of a given size normally will be greater near a small rural community than near a large urban area. This generally is due to the fact that a small rural community is likely to have a nonmanufacturing economic base and a lower per capita income, fewer social groups, a more limited socioeconomic infrastructure, and fewer leisure pursuits than a large urban area. There are situations, however, in which the changes in a small community may not be significant, and conversely, in which they may be considerable in an urban area. For example, a small community may have had a manufacturing (or natural resource) economic base that has declined. As a result, such a community may have a high incidence of unemployment in a skilled labor force and a surplus of housing. Conversely, a rapidly growing urban area may be severely strained to provide the labor force and services required for a new phosphate facility.

The rate at which changes occur (regardless of the circumstances) also is often an important determinant of the significance of the changes. The applicant should distinguish clearly between those changes occasioned by the construction of the facility, and those resulting from its operation. The former changes could be substantial but usually are temporary; the latter may or may not be substantial, but normally are more permanent in nature. The potential impacts which should be evaluated include:

- Increased consumption and rate of land development.
- Land use pattern and compatibility changes.
- Economic base multiplier effects.
- Population size and composition changes.
- Increased labor force participation and lower unemployment rates.
- Increased vehicular traffic and congestion.
- Loss of prime agricultural land and environmentally sensitive areas.
- Increased demand for community facilities and services.
- Increased demand for water supply, sewage treatment and solid waste disposal facilities.

During the construction phase, the impact will be greater if the project requires large numbers of construction workers to be brought in from outside the community than if local unemployed workers are available. The potential impacts include:

- Creation of social tension.
- Short-term expansion of the local economy.
- Demand for increased police and fire protection, public utilities, medical facilities, recreation facilities, and other public services.

- Increased demand for housing on a short-term basis.
- Strained economic budget in the community where existing infrastructure becomes inadequate.
- Increased congestion from construction traffic.

Various methods of reducing the strain on the budget of the local community during the construction phase should be explored. For example, the company itself may build the housing and recreation facilities and provide the utility services and medical facilities for its imported construction force. Or the company may prepay taxes, and the community may agree to a corresponding reduction in the property taxes paid later. Alternatively, the community may float a bond issue, taking advantage of its tax-exempt status, and the company may agree to reimburse the community as payments of principal and interest become due.

During operation, the more extreme adverse changes of the construction phase are likely to disappear. Longer run changes may be profound, but less extreme, because they evolve over a longer period of time and may be both beneficial and adverse.

The permit applicant should document fully in the EID the range of potential impacts that are expected and demonstrate how possible adverse changes will be handled. For example, an increased tax base generally is regarded as a positive impact. The revenue from it usually is adequate to support the additional infrastructure required as the operating employees and their families move into the community. The spending and respending of the earnings of these employees has a multiplier effect on the local economy, as do the interindustry linkages created by the phosphate facilities. The linkages may be backward and forward. Backward linkages are those of the facility's suppliers. Forward linkages are those of the facility's markets.

Socially, the community may benefit as the increased tax base permits the provision of more diverse and higher quality services, and the variety of its interests increases with growth in population. Contrastingly, the transformation of a small community into a larger community may be regarded as an adverse change by some of the residents who chose to live in the community, as well as by those who grew up there and stayed because of its small town amenities.

The applicant also should consider the economic repercussions if, for example, the quality of the air and water declines as a result of various emissions from the phosphate facility. In some cases, other more traditional sectors of economic activity may decline because labor is drawn away from them into higher paying phosphate related or tertiary sector activities. As an illustration, the fishing sector may decline if water pollution increases, or if fishermen abandon the occupation in favor of employemnt at the phosphate facility. Again, the tourist sector may decline if air and water pollution is noticeable or if the landscape is degraded.

Thus, the applicant's framework for analyzing the socioeconomic impacts of the location of a phosphate facility must be comprehensive. Most of the changes described can and should be measured to assess fully the potential costs and benefits. The applicant should distinguish clearly between the short-term (construction) and long-term (operation) changes, although some changes may be common to both (e.g., the provision of infrastructure). The significance of the changes depends not only on their absolute magnitude, but on the rate at which they occur. The applicant should also develop and maintain close coordination with State, regional, and local planning and zoning authorities to ensure full understanding of all existing and/or proposed land use plans and other related regulations.

US EPA's Office of Federal Activities is developing a methodology to be used to forecast the socioeconomic impacts of new source industries and the environmental residuals associated with those impacts.

5.0 EVALUATION OF AVAILABLE ALTERNATIVES

The alternatives section of the EID should address each reasonable alternative equitably. The purpose of this analysis is to identify and evaluate alternate plans and actions that may accomplish the desired goals of the project. These alternatives can include process modifications, site relocations, project phasing, or project cancellation.

For the alternatives to a proposed project to be identified and evaluated properly, the impact assessment process should commence early in the planning phase. In this manner, social, economic, and environmental factors against which each alternatiave is to be judged can be established. Cost/ benefit analysis should not be the only means whereby alternatives are compared. The environmental and social benefits of each alternative also must be considered. In general, the complexity of the alternative analyses should be a function of the magnitude and significance of the expected impacts of the proposed processing operations. A small operation that uses purchased raw materials or existing by-products may have a relatively minimal impact on a region and generally would require fewer alternatives presented in the EID.

The public's attitude toward the proposed operation and its alternatives also should be evaluated carefully. In this way key factors such as aesthetics, community values, and land use can be assessed properly.

5.1 SITE ALTERNATIVES

The phosphate fertilizer industry locates facilities on the basis of convenience to raw materials, an adequate labor force and water supply, proximity to energy supplies and transportation, minimization of environmental problems, and only to a limited extent on the basis of market demand and other factors. A variety of sites initially should be considered and, following a detailed analysis of each one, a preferred alternative should be selected that appears to satisfy the objectives and that is expected to result in the least adverse environmental impact. When the site is planned in the mining area, the selection factors will also be related to mining impacts and any integration possible for processes, handling systems, and common waste disposal sites and treatment techniques.

The factors considered in selecting each site, and especially those that influenced a positive or negative decision on its suitability, should be carefully documented in the permit applicant's EID. Adequate information on the feasible alternatives to the proposed site is a necessary consideration in issuing, conditioning, or denial of an NPDES permit (40 CFR 6, Subpart F). Proposals to build in areas of steep terrain, unstable soils, wetlands or high water tables, and urbanized areas should devote comprehensive analysis to siting alternatives.

Specifically, the advantages and disadvantages of each alternative site must be catalogued with due regard to preserving natural features such as wetlands, coastal zones, and other sensitive ecosystems and to minimizing use of flood plains or other areas of significant adverse environmental impacts. The applicant should ascertain that all impacts are evaluated as to their significance, magnitude, frequency of occurrence, cumulative effects, reversibility, secondary or induced effects, and duration. Accidents or spills of hazardous or toxic substances vis-a-vis site location should be addressed.

When a proposed site is controversial, it may have to be abandoned for a number of reasons. Such opposition may derive from the fact that the proposed facility would significantly impact a unique, recreational, archaeological, or other important natural or man-made resource area. It may destroy the rural or pristine character of an area. It may conflict with the planned development for the area. The site may be opposed by citizen groups. It may have to be discarded for meteorological and climatological reasons. It may be subject to periodic flooding, hurricanes, earthquake, or other natural disasters.

If the proposed site location proves undesirable, then alternative sites from among those originally considered should be reevaluated, or new sites should be identified and evaluated. Expansion or continued use of an existing facilities site also could be a possible alternative solution. It is critical that a permit applicant systematically identify and assess all feasible alternative site locations as early in the planning process as possible.

5.2 ALTERNATIVE PROCESSES DESIGNS, AND OPERATIONS

Typically, when the decision is made to expand manufacturing capacity--either through a new plant or an addition to an existing one--the type of facility to be constructed is already fixed; that is, the demand for phosphoric acid and/or other end products would have dictated the general types of processes to be used. The limitation on process alternatives is not as severe as it once was in dry products because of improved versatility of granulation processes.

In addition to demand, the process alternatives should be selected on the basis of availability and quality of required raw materials as well as environmental considerations. The applicant should present clearly and systematically in the EID the methodology used to identify, evaluate, and select the preferred process alternatives. In unusual cases where water supplies or raw materials quality is a constraint or land availability of concern, process alternatives now only in research or pilot plant stages may be considered by the applicant. For example, the thermal process for phosphoric acid would eliminate gypsum-pond-related waste problems, but it has other solids disposal problems. Other alternatives continuously being investigated include solvent extraction of wet process acid impurities and use of alternate acids to produce alternate fertilizer products directly from phosphate rock and eliminate gypsum wastes (although other wastes may pose other serious difficulties).

5.3 NO-BUILD ALTERNATIVE

In all proposals for facilities developed, the applicant must consider and evaluate the alternative of not constructing the proposed new source facility. Because this analysis is not unique to the development of phosphate fertilizer manufacturing facilities, no detailed guidance is provided as part of this Guidelines document. The permit applicant is referred to Chapter IV (Alternatives to the Proposed New Source) in the document, Environmental Impact Assessment Guidelines for Selected New Sources Industries (USEPA 1975). The no-build alternative in the present context can include sale of raw materials to existing facilities in instances where an applicant produces one or more of the raw materials for phosphate fertilizers and where transportation impacts may be less severe than impacts of siting a new source phosphate manufacturing plant in the proposed area.

6.0 REGULATIONS OTHER THAN POLLUTION CONTROL

The applicant should be aware that there may be a number of regulations other than pollution control regulations that have some application to the siting and operation of new phosphate fertilizer manufacturing facilities. The applicant should coordinate with the appropriate USEPA Regional Administrator regarding applicability of such regulations to the proposed new source. Federal statutes which generated regulations that may be pertinent to a proposed facility include:

Council of Environmental Quality, Rules and Regulations for NEPA, Implementation of Procedural Provisions (40 CFR 1500, rev. Nov. 29, 1978)

Environmental Protection Agency, Implementation of Procedures on the National Environmental Policy Act (40 CFR 6, November 6, 1979)

Coastal Zone Management Act of 1972

The Fish and Wildlife Coordination Act

The National Environmental Policy Act of 1969

USDA Agriculture Conservation Service Watershed Memorandum 198 (1971)

Wild and Scenic Rivers Act of 1969

The Flood Control Act of 1944

The National Flood Insurance Act of 1968

The National Flood Disaster Protection Act of 1973

Federal-Aid Highway Act, as amended (1970)

The Wilderness Act (1964)

Endangered Species Preservation Act, as amended (1978)

The National Historical Preservation Act of 1974

Executive Orders 11593, 11988, and 11990

Archaeological and Historic Preservation Act of 1974

Procedures of the Council on Historic Preservation (1973)

Occupational Safety and Health Act of 1979

Safe Drinking Water Act, as amended (1977)

Atomic Energy Act

In connection with these regulations, the applicant should place particular emphasis on obtaining the services of a recognized archaeologist to determine the possibilities of disturbing an archaeological site, such as an early Indian settlement or a prehistoric site. The National Register of Historic Places also should be consulted for historic sites such as battlefields. The applicant should consult the appropriate wildlife agency (State and Federal) to ascertain that the natural habitat of a threatened or endangered species will not be adversely affected.

7.0 REFERENCES

The literature references listed in this section include cited references and additional selected bibliographic references. The listings immediately below are short form citations arranged according to topics. A complete listing of full references, arranged alphabetically, follows the short form citations. These citations are useful for further information in specific topic areas.

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